The Manufacture of

LAKES

and Precipitated

PIGMENTS

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The
MODERN
CHEMICAL INDUSTRIES
SERIES

General Editor

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THE MANUFACTURE
OF
LAKES
AND
PRECIPITATED PIGMENTS

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The
MODERN CHEMICAL INDUSTRIES SERIES

General Preface

The present work belongs to a series of handbooks published under the general title of The Modern Chemical Industries Series The aim of these books is to give a clear, straightforward description—written from a technical standpoint—of present-day manufacturing operations and their scientific control

The scope embraces modern plant and practice only Special attention is given to the methods and equipment used in evaluating materials and controlling processes The authors, in each case, are men of recognised technical ability, with actual works experience

Special precautions are taken to avoid the inclusion of obsolete processes and matter of purely scientific or historical interest On the other hand, equal care has been taken to avoid anything approaching the " catalogue " style The books are intended to embody the experience of industrial chemists gained in every-day practice

Each volume is devoted to a single industry, or group of related industries, and the final volumes will include a General Index to the whole series They will also include such additional matter as is required to ensure the series being a self-contained Library covering the entire range of the chemical and allied industries This arrangement confers a flexibility which enables additions and revisions to be made when and where required ; it ensures—and this is vitally important to technical literature—a continuous growth in the most economical manner possible

H B Cronshaw.

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The Manufacture of
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PIGMENTS

Preface

THE present book deals with the manufacture of a number of coloured pigments, which though chemically diverse are produced by similar processes and used in the same industries, and are therefore invariably made in the same works

Of these the pigments derived from synthetic organic dyestuffs (generally termed "lakes") form by far the largest groups so far as numbers are concerned, but the lead chromes and prussian blues and allied colours are industrially equally important

The essential operations involved in the manufacture of these pigments are solution, precipitation, drying and grinding. In the laboratory these are fairly simple processes, but in the works many complex problems arise, both economic and technical, and the success of the colour chemist depends largely upon his ability to appreciate the nature of the problem and the standards by which his product will be judged. This indeed is the most difficult part of the chemist's task The value of a pigment depends ultimately upon a variety of physical properties, many of which are not definable in strictly scientific terms Consequently a knowledge of the industries using pigments and the standards by which his products are judged is an essential part of the chemist's and works manager's training

These properties are largely determined by the chemical and physical conditions under which the pigments are produced. Factors which in ordinary laboratory operations are of comparatively little importance become vital, and consequently the colour maker needs all the resources of science in order to attain success

The production of a pigment on a large scale must indeed be regarded as a scientific process in many ways more delicate than the corresponding operation conducted in the laboratory with a few grammes of material.

In this respect the works process performs a function analogous to that of the microscope—slight differences are magnified and become all-important, and subtle variations in the properties of the product are revealed when it passes under the examination of men who have long and intimate experience of its use in highly specialised industries

One is thus early made to realise that the formation of a coloured precipitate is merely the first step in the preparation of a product which will satisfy the demands of the pigment users

On the purely technical side these difficulties are mainly due to the fact that the properties of the product to which so much importance attaches are greatly affected by the conditions of manufacture—questions of temperature, concentration, rate of stirring, and time of settling are of vital importance

These questions do not arise to any great extent in laboratory operations, and even when they are specially investigated on a laboratory scale, the widely different conditions on a works scale render it necessary to repeat the processes on at least a semi-works scale in order to discover the best conditions for producing the desired result

When, therefore, Mr Harrison was approached on the subject of this book he was asked to base it upon his own experience as a lake maker, and to assume that the reader has a sound knowledge of the principles of chemistry, physics and mechanics, and was therefore able to use intelligently the many excellent textbooks and original articles available in any reasonably well-equipped works library, and to concentrate on those matters which do not fall within the scope of such works.

The object of the work is therefore two-fold—on the one hand it is essentially practical in that it deals with the processes as a means of producing a satisfactory saleable article, and on the other it is intended to emphasise the importance of strictly scientific methods in the works

The manufacture of a pigment is in fact considered as being a scientific operation in some respects even more delicate than the corresponding laboratory experiment, for as already pointed out, many factors comparatively unimportant in the laboratory become of vital importance in the factory In the past this difference between works practice and laboratory experiment has been the chief rampart in the defence of the "practical man with his secret process" against the intrusion of the scientist

Mr Harrison writes as a chemist who has penetrated the rampart and has emphasised the fact that the successful control of every stage of the processes involved is essentially a task for the scientifically trained man, and that although our knowledge of the chemical and physical factors involved is by no means yet complete, strict attention to detail and minute and accurate observation based upon a sound grasp of scientific fundamentals are the only real secrets of success

It is hoped, therefore, that this book will not only prove helpful to those directly concerned with the industry in question, but also to the general student of science

Apart from their importance to the industry itself, the problems dealt with have a purely scientific significance, and their study by the academic worker also cannot fail to prove of value both in contributing to the store of exact knowledge and in suggesting new developments and applications of scientific theory.

T Hedley Barry.

May, 1930.

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THE MANUFACTURE OF LAKES AND PRECIPITATED PIGMENTS

CHAPTER I

INTRODUCTION

IN writing this book, the author has set out to produce a work on essentially practical lines, in which practical working methods, as well as useful hints for guarding against difficulties and breakdowns, have been as fully treated as possible Some of the special hints and cautions about practical manipulation of colour batches, and special arrangements of little details that count for efficiency in the plant, and installation, are from the author's own first-hand experience, and many of them have been generously contributed by personal friends who are well-known practical pigment colour makers

More attention has been paid to describing fully such practical details of works and plant arrangement, and personal skill and observation, in making works batches and tests, as are essential to success, than has been given to actual formulæ for colour making The author considers that lists of actual formulæ on paper are almost valueless, except to the highly skilled worker—who, incidentally, will have a very useful range already at his command Such formulæ as are required, that depend on the use of special dyestuffs, can always be found in the very useful and comprehensive books issued by the pigment dye-making firms (as for example the booklet "Colour Lakes," issued by Imperial Chemical Industries, Limited, or "Dyestuffs for Lake Manufacture," issued by the Clayton Aniline Co., Ltd)

These will enable any good practical worker to make up pigments quite successfully from the respective dyes mentioned They are excellent handbooks and no chemist or practical man producing lakes and pigments from dyes should be without a copy. Although this type of trade handbook is very thorough and accurate, it obviously cannot give much practical information about working difficulties and unforeseen "snags" in actual processes, and will quite naturally be compiled with a slight bias in favour of the particular firm's products

In the chapters where actual processes are given for making lakes from dyes (Chaps. XIV to XXIV) a few typical examples of each class have been given. No attempt has been made to give lengthy and comprehensive lists of so-called "formulæ" Instead, more space has been devoted to a full description o general manipulations, difficulties encountered and rules to observe In deciding on any individual dyestuff, the colour maker can readily obtain full details of all recommended quantities and methods of preparation from the makers of the dye For the same reason, only a few typical dyes of each group with their main properties have been given at the end of the corresponding chapters Exact shades and general properties obtainable with the whole range of their products, are always obtainable from the various large dye manufacturers

The object, then, of this book is to fill a distinct gap between manufacturers' publications and chemical textbooks, and offer the skilled chemist or technical man a reliable practical work of reference, from which he can compare and confirm his own knowledge and theories, and pick out additional practical hints from the experience of others. The book is intended, above all, to serve as a textbook for the junior chemist or technical man, to whom it should prove useful in furnishing actual details of work, and enabling him to foresee and provide for many small difficulties which are encountered in the actual working of processes. Of necessity, many things of an elementary nature have been included, and no apology is offered for this, as some of these very elementary details and safeguards have a tendency to become over-familiar to the skilled man, and so lose their importance, while to the beginner or partly experienced worker they cannot be too much stressed

References have been added wherever they appear usefu or necessary, but as far as possible these have been confined to English works and those that are more readily accessible to the average pigment maker or colour chemist It is not out of place at this point to make special mention of the very varied and useful work that is done and published by the Oil and Colour Chemists' Association in their monthly journal, and so well indexed in their yearly index. If full use be made of the reports of lectures and papers and subsequent discussions in these monthly publications, many useful practical hints will be gained

Other works which are exceptionally useful in their various spheres and are well within the means of the works chemist are·—

1. "The Chemists' Year Book" F. W Atack
2. "The Analysis of Pigments, Paints and Varnishes." J. J Fox, O.B E., D Sc, F.I.C, and T H Bowles, F I.C
3. "The Scheme of Analysis for Detection of Dyestuffs in Finished Pigments." Prof A G Green
   (Oil and Colour Chemists' Assoc Journ, Vol XI., No. 92, pp 38-48)

A few special definitions are given, purely from the author's viewpoint, for the purposes of this book only ·—

PIGMENT

Any coloured substance, more or less opaque, relatively insoluble in the particular vehicle in which it is to be used

LAKE

Any coloured substance, produced by the precipitation of an organic dyestuff, more or less translucent, insoluble in the particular vehicle in which it is to be used, and non-bleeding in water

GLAZE

Similar to a lake colour, but more transparent.

SUBSTRATUM OR BASE

Any insoluble substance, opaque or translucent, coloured or otherwise, used as a foundation on which to precipitate the colouring matter.

COLOUR

It must be constantly borne in mind that colour is not a concrete, inherent property of any substance, it is rather the *effect* on the eye which any substance produces under the given circumstances, and is not therefore a standard property for an individual substance *except* under exactly repeated standard conditions Two useful examples showing this variation are —

1. Any bright red, or other coloured *dry* powder, even when smoothed out flat under a palette knife, shows a totally different shade and colour when wetted down with a colourless liquid such as refined benzine, owing to the modification brought about by the difference between the refractive value of the liquid and that of air

2 A light red surface, viewed through a pale blue glass, will appear purple, through a pale green will appear brown, through a yellow glass will appear orange, whilst if other coloured objects be placed on it and it then be viewed through a suitable tinted red glass, will appear almost white. It is obvious from this that colour in an object is not concrete, but very variable and quite a relative property, except under specified conditions It is obvious that colour itself is to be considered as a purely physical phenomenon, but this point is given special and primary importance in view of the fact that most of the desired modifications and exact effects of texture, shade, appearance, undertone and surface in a given chemical formula for a coloured substance are mainly dependent on physical considerations, governed by the physical conditions throughout the processes, and resulting in differences in size, shape and density of the particles, and in allotropic modifications, amorphous and crystalline, for example, "bronzy" or "reflex" varieties of pigments consist of ultra-fine definite *crystals* of the pigment in question.

So much depends on these various physical properties that an essential qualification for a successful pigment colour maker is a constant and accurate faculty of observation This should be cultivated and trained at every opportunity by the beginner if he wishes to become a reliable and expert man (General remarks on this point have been made by the author in his paper "Lake Dyestuffs and their Application," *vide* Journal of the Oil and Colour Chemists' Association, Vol X, No. 80, pp 28-39)

SECTION 1

FACTORY DESIGN AND EQUIPMENT

CHAPTER II

FACTORY LAYOUT

THE quality and uniformity of the products of a pigment colour works and their production on an economic price footing will be found to depend largely on the factors dealt with in this chapter. Although the average chemist or colour maker will not usually need to concern himself with initial planning, layout and installation, yet these are items with which he should be conversant, if only to enable him to have the knowledge and take interest in watching over all these points, so that he may advise and assist in bringing existing conditions to a more efficient or workable level where this appears necessary Some of the minor practical suggestions are such as can be adapted or used by the individual worker in his own special units of plant. Where the chemist is given full working control of mechanical arrangements, he should carefully weigh up the advantages of various systems, and in cases where obsolete plant or arrangement are obviously causing loss or lack of reliability, he should draw up a proper plan and scheme of necessary modifications, on the least costly basis possible, and place the facts in a clear manner before his employers This particularly applies to a chemist in full charge, for it sometimes happens that a chemist so placed will hesitate to ask for any expenditure, however sound and necessary it may be , this attitude is a weakness too often encountered, but it does jeopardise both his own and his employer's future success

In the case of a chemist collaborating in the extension of a works or in the erection of new premises and plant, or even in taking over old premises to be adapted for his own range of processes, the general principles dealt with in this chapter are of first importance. He should also gather all information possible on these various points from reliable authorities on specialised subjects, such as drainage, tanks, ventilation, heating, drying, grinding, etc , as well as avail himself of the expert knowledge to be obtained from the engineers of well-known makers of the special installations concerned.

Another aspect of the question is, that a practical knowledge of desirable types of layout and installation, types of plant and power, etc., can be employed advantageously in replacing or renewing sections of existing plant, or in installing new units The practical man who has a keen interest in the mechanical side can at such times co-operate, and often save much time and money, by guarding against breakdowns, and by increasing the efficiency of output. A first-class colour chemist will, of necessity, have a sound knowledge of the mechanical and engineering side of his business, this being a side that can very easily absorb all profits, unless given full attention and care. The beginner may very usefully memorise a sound maxim and be guided by it in his conduct—breakdowns are *costly*.

Water Supply. The first consideration for a pigment colour works is a suitable site or locality, which must be so chosen that an abundant and assured supply of the right kind of water, at a reasonable cost, is available. Any natural sources of water (artesian well, river or stream) should be quite free from iron for all colour work, and some knowledge of the ground through which the water passes is advantageous Such a source of supply should not vary too widely in saline content and hardness from season to season, unless specia means are adopted to rectify the variation, and it should at all times be quite free from iron Magnesium, often found to a moderate extent in natural waters, is not so harmful as iron but being difficult to remove, and very undesirable in making madder lakes and bright basic, dye lakes, it is better to rely on water relatively free from magnesium. If the water contains excessive temporary hardness this can be removed in a simple type of water-softening plant Once a water of certain composition and degree of total saline contents has been successfully used and accepted, then for all large scale work of importance, especially with bright lakes, this should be adhered to as nearly as possible.

Water drawn from a well or stream should be absolutely freed from suspended matter, the usual process adopted in colour works being filtration through a series of graduated copper sieves of large cross-sections, and finally draining from the top of a settling tank.

Effluent The provision of an adequate effluent system and its maintenance in efficient working order is a matter of firs importance Steps should be taken to find out exactly how, and by whom, the effluent will be controlled, and the official regulations as to permitted percentages of various "solids" in the effluent where it joins the local system In any case large settling pits (brick-lined), in a series of at least two, should be included in the works drainage system , this allows the first to be used for settling out the major part of solid suspended matter, whilst in the second, preferably at some distance away, the run-off liquors will become averaged out with cleaner washing water and will deposit any remaining suspended matter One system is to have underground glazed-brick settling vats, situated beneath or near to the main colour making vats, where such heavy colours as chrome yellows and greens and cheap, reduced grades of reds or blues are regularly made They should be of ample size and easily accessible, each one of the settling vats being kept for the effluent from groups of very similar shades With this system it is necessary to remove the settled-out colour at regular intervals From these primary settling tanks quantities of off-shade mixed colours of fine texture can be recovered, at least in sufficient quantity to pay for the expense of cleaning out and the upkeep of the settling tanks

These primary settling tanks must always be supplemented by others further away in the system

Where plenty of waste ground with a sandy subsoil is available on the site, some use can often be made of a "soakaway" drainage to eliminate at least a part of any undesirable and high saline content Any individual processes giving particular trouble in this respect should be run to an independent branch and settling-out system, to be dealt with before joining the main effluent The chief difficulties will be encountered in populous districts and where the effluent is near to a main drainage running to a sewage-farm or small river. In one works the author visited, on an old colliery property, a disused mine working was very effectively used to dispose of all the worst effluent

The whole question of works drainage is to be considered as part of the effluent problem, and starts, properly speaking, with the flooring in the buildings where presses and vats are situated. In these places provision must be made for a continual flow of water on the floors, for there will be a moderate amount of water about from hosing down vats, presses, filter cloths, etc , as well as accidental leakages and overflows All such floors should have a proper fall or slope to the gutters or drains, and a good plan where space permits, at least in the filter-press room, is to have a slight fall from the centre to either side of the building, along which gutters can be run, covered in with cast-iron gratings The plan used in some small shops, viz., a " square cone " type of fall, from the four sides to a drain in the centre, is to be deprecated, as it gives too great a flow at times to one easily blocked point.

All actual drain-pots and sumps should be kept constantly covered with grids and should be arranged to give a proper fall to all pipes throughout the system, and all runs so arranged that the system can be easily cleaned in sections with drain-rods. Where large volumes of effluent are to be dealt with, it is important that the main runs outside the buildings be easily accessible, and if possible, so arranged as to permit of easily opening-up the ground to attend to leaky sections or permanent blockages if they occur, as inevitably happens even in the best regulated works In making up any temporary runs in works, whether surface (half section gutters) or runs of pipe to a sump, care should be taken to see that all laps and joints run in the right direction, so as to avoid undue erosion of the cement or jointing, and excessive leaking when the joints do fail

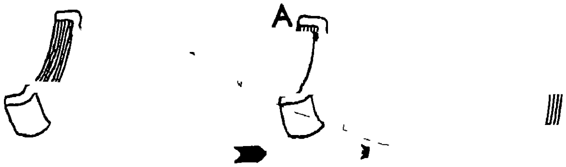

FIG 1—Correct Method of Lapping Open Drain Joints Arrow shows direction of fall of drainage A indicates acid-proof cement joint

Accidental stoppages due to wooden bungs, rags, or other debris, are most likely to occur in the first sections of drainage inside the works The system which affords the greatest safeguard is that of deep open channels, covered with iron gratings , these are easily accessible and will often save troublesome delays.

The first run-off liquors from most of the ordinary types of pigments contain fairly high percentages of saline matter,

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generally consisting of some of the following: sulphates, nitrates, chlorides and acetates of sodium and potassium, and small percentages of acetic and mineral acids; these first saline liquors have far more action on ordinary mortar and cement than the later washings, and so should be carefully prevented from running on to ordinary brick and mortar foundations of walls, vat-supports, etc. In view of their action on ordinary cement, all joints in drainage systems should be made a good flush fit and preferably with acid-proof cement. This is far more necessary when the nature of the process involves an acid first-run-off. "Mother liquors" containing free sulphuric acid with chlorides of sodium, potassium, or ammonia are particularly harmful owing to the free hydrochloric acid present in them.

Where a number of large scale processes are carried on simultaneously and regularly, it is of course bad practice, both from the point of view of wear and tear, and the proper control of effluent, to arrange the processes so that several large vats are given their first (and most heavily charged) run-off at the same time. When it can be arranged to run off one or two later washings from other vats simultaneously with a more saline first washing, very little difficulty will be encountered with the effluent.

When using a system of large underground collecting and settling vats for the first washings (having a slow rate of overflow to the main drains), it can be arranged to run at least some of the later washings to a separate branch, to mix with the more saline washings at an early point in the main drains, or even better, in a second settling and mixing sump of large dimensions before they both reach the main system.

Transport. The products of most pigment works amount to enormous weights in the year, and therefore the question of accessibility of the main markets and costs of transport must have a considerable influence on the choice of a site.

This applies also to the cost of bringing raw materials into the works; in this connection, acids, salt, alkali, barytes, coal, etc., can often be most cheaply brought in by canal or river. These considerations apply more particularly to works having a big staple output of heavy mineral colours of the cheaper grades. Where smaller weights of fine lake colours of low gravity and relatively high value only are made, this question of transport has far less bearing Accessibility of markets can best be ensured in these cases, not so much by locality, as by carrying reasonably large and varied stocks of finished products, or by the establishment of smaller stock depots in suitable centres

Power. Another important factor in determining the suitability of a locality or site is that of the cost of power and whether adequate power at a low cost is available in the form of coal or electricity for all present and future requirements.

If a proposed site or existing works or building includes space for future extensions, that is an important advantage.

Factory Layout With regard to the buildings themselves, in an efficient colour works these should include mostly two- or three-story workshops of the " gallery " type, as this arrangement allows the passage of most of the materials from one stage of a process to another, by gravitation. In the rooms where vats or other tall pieces of plant are fixed, there should be as much head-room as possible to permit proper working and observation, and still allow the vats to stand several feet clear of the floor (some air-space under the vats is essential to prevent rotting). This last arrangement is very desirable as it allows a good head of colour to a pump feed when filtering in presses on the same floor, or a direct run-off of the wet colour into vacuum filters when filtering heavy granular colours in open vacuum filters The latter is a very rapid and cheap method of filtering for colours of a suitable type. Where heavy raw materials and finished products are concerned it is almost essential to have a good power-driven lift or hoist, so placed as to deal with most of the heavy raw materials Very heavy stocks required in big quantities are best stored in a very accessible place on the ground floor, convenient for receiving into the works and close to the hoist or other means of delivery to the place where they will be actually used. It generally pays to put in a few small wall-crabs or hand-winches, bolted to the wall, for smaller but regular lifting operations in awkward or cramped situations ,—they take up very little space, and soon pay for their cost in saving time and labour

Ventilation. Efficient ventilation will always pay for itself in a workshop where steam and chemical fumes are constantly being evolved. The worst processes in this respect can generally be performed in sheds or hangars open on one side, or in buildings with the fullest provision for ventilation in the roof and sides Where these conditions are not obtainable, then to minimise costly wear on light and power fittings, on belting and machinery, on the buildings and roofs, a sufficiently large stream-line fan should be provided in one of the walls (near the roof, if possible) and preferably *to deliver* into the outer air, away from other buildings and habitations, *but* in the direction of the local prevailing winds

Most of the generally desirable requirements so far mentioned, in connection with new sites or the extension and improvement of existing works, are equally important when considering the suitability of an old site and building to be utilised for making pigment colours. Such things as drainage, water-supply, two- and three-story workshops (at least in part), reasonable facilities for receiving raw materials and delivering products to the consumer, an adequate amount of head-room and good floorings and foundations in the works, must all be in accordance with proper requirements, or capable of being adapted *cheaply,* otherwise the enterprise starts with too big a handicap Many sites or buildings that otherwise would be quite suitable, are quite unfitted for such work, owing to lack of sufficient drainage systems or to bad and unsuitable floorings

CHAPTER III

PLANT AND INSTALLATION

(1) *Vats, Stirring Gear, Pumps, etc*

(2) *Drying Systems and Grinding Systems.*

THE actual choice of plant and machinery, and its proper installation, will be largely governed by the range of products that are to be made and the scale on which operations are to be conducted There is, however, a number of general considerations which can be studied with advantage, whether for large-scale or medium-scale work

The question of floorings, drainage, etc , has been briefly referred to in Chapter II, pages 7 and 8, and the scope of this book does not allow of more detailed comments.

VATS

The first item should be the vats for the various processes to be worked Even if only working on a small scale, one or two vats of large capacity should be provided to permit making big batches when suddenly required, or making very dilute bulky batches of special colours, such as alumina lakes

(*a*) *Material* The most generally useful vats for average pigment colour works are made from good close-grained pitch-pine , the best type of hoops being round-section iron with special nut and clip fastenings, as illustrated in Fig 2 These round-section hoops can be much more readily cleaned-up and re-painted, and can be made to withstand corrosion and rusting much longer than the ordinary flat-section hoops

Spruce-fir vats are much used on the Continent where this wood is abundant Very excellent, cheap vats can be made of this wood They are easy to keep water-tight if maintained in good condition, but have the disadvantage of being structurally weaker than pitch-pine, and less resistant to weak acids and alkalis They tend to become very porous and so can only be used successfully for regular runs of one colour, owing to their tendency to retain material in the porous inside surfaces Oak vats are very strong and durable, and will stand a lot of boiling-up, but they should not be used for any delicate colours, as they so readily give bluish stains, with even minute traces of iron Lead-lined vats (made of any of these woods) are generally used for operations where long boiling-up is necessary, or where distinctly acid liquors (*other than those containing hydrochloric acid or chlorides*) are to be used Examples are, the coupling up of azo-pigment dyes, making of diazo-compounds for these, also the oxidation of iron-blues and ferrite yellows, and the preparation of strong solutions of chemicals (as for instance strong solutions of bichromates, which would soon ruin a wooden vat)

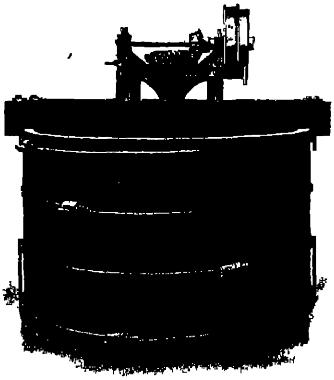
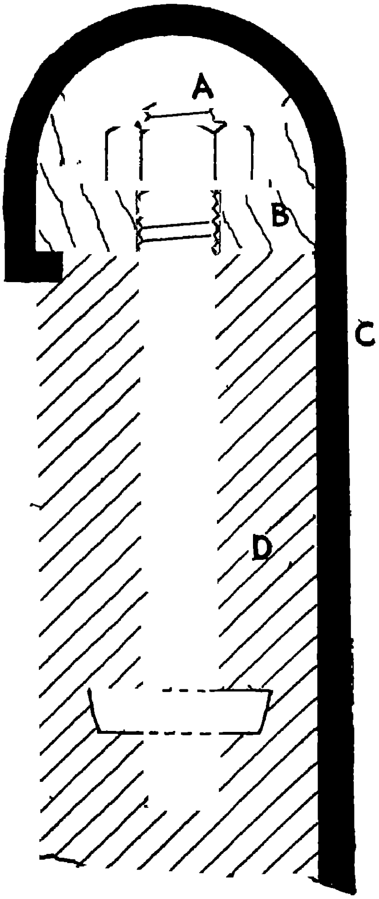


Fig 2 —Simple Type of Vat and Gearing Illustrating Special Type of Hoops and Hoop-Fastening (*see* page 12)
(*By courtesy of S H Johnson & Co, Ltd*)

For the manufacture of lead nitrates other materials have to be used, the alternatives being glazed acid-resisting earthenware, or granite, or special linings of vulcanite or hard rubber In the colour works where pigment dyes are also made from intermediates, care should be taken not to use wooden vats for highly nitrated compounds.

(*b*) *Size and Shape* Another important side to the question of vats is their actual shape and proportions, which may be almost as varied as the number of uses to which they can be put. It is best on this account to give a number of typical examples, which will cover most usual cases.

Tall cylindrical vats of relatively narrow width, with spirally arranged agitators, are most suitable for the manufacture of such colours as oxy-chloride chromes, or for mixing pulp colours in paste form to a uniform strength, or in fact any operation where good mixing of heavy material is required with a slow steady movement, and where ingress of air is not necessary or is undesirable.



A	Holding-down bolt in recess in wooden coping
B	D-shaped wooden coping
C	Interior lead-sheet lining of tank
D	Cross-section of cement tank-wall

FIG 3 —Mode of Attaching Lead-Sheet Lining to Cement Tank-Wall (*see* page 15)

The reverse type, where rapid mixing of materials of lower gravity is required (with a maximum of surface-exposure to air), is the shallow wide vat with a broad cross-beam type of stirrer blade near the bottom of the vat. A square vat is useful for very efficient "beating-up," as, for example, in making an insoluble diazo-compound where fine subdivision is needed.

Large vats for storage of *neutral* and comparatively inert saline solutions can be economically built from bricks with a good cement-and-sand mortar The best bricks are "brindled blue"—these are rough enough to knit well together and yet not porous In building such tanks good sound workmanship is necessary and all courses should be half-jointed, and for 9-in. thick walls in two 4½-in layers, liberal cross-keying with end-on bricks should be employed

Much better tanks, more reliable than brick ones, can be built from concrete, reinforced with iron rods These make a very good job for four- or eight-sided tanks such as are used for neutral saline liquids (not chlorides) or for water storage, while they are ideal for making lead-lined vats of big capacity owing to the smooth finish of the interior. Irregularities under the lead coating cause rapid wear and piercing of the lead lining When planning such vats for lead lining, a wooden "coping" must be fitted to which to attach the lead, the surest attachment being as shown on page 14.

Any cement vat is best built by a firm which specialises in this class of work and sends its own men to carry out the work As a general guide for thickness of materials necessary the following will serve as a useful basis —

	OAK	SPRUCE	PITCH PINE
Capacity 500 gallons .	1½ in	2 in	1½ in —2 in
,, 2,000 ,,	2 in	3 in	2½ in —3 in.
,, 5,000 ,,	3 in	(not advisable).	3½ in

In each case the bases are best slightly thicker

LEAD LINING.

APPROXIMATE CAPACITY OF VAT.	LEAD, LBS PER SQ FT
500 gallons	6 lbs to 8 lbs
1,000 to 2,000 gallons	8 ,, 10 ,,
2,000 ,, 5,000 ,,	10 ,, 12 ,,

The heavier weight of the two is always the more desirable Pure chemical sheet-lead only should be used.

VAT FITTINGS AND VAT EMPLACEMENTS

(*a*) *Stirring Gear* Gearings for stirrers are usually fitted on a cross-balk of pitch-pine or other timber, and a smooth piece of pitch-pine is by far the best, as it allows easy cleaning down, whilst rough, softer wood encourages the accumulation of old colour, rust, dirt, etc It is quite a mistake to fit agitating gear on steel girders across the vat for anything but unimportant dull colours

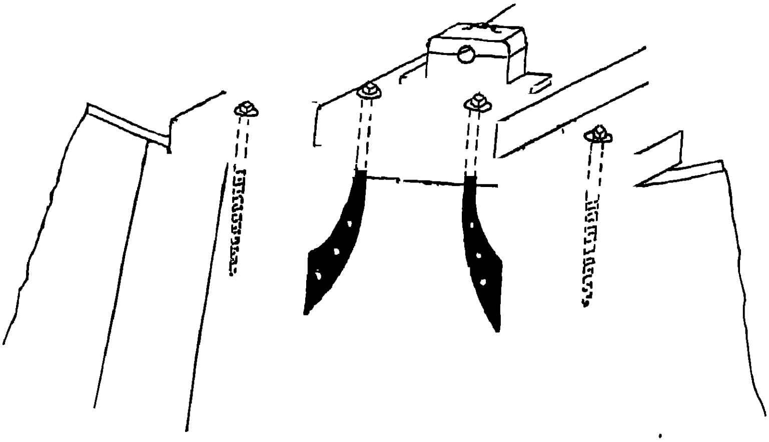


FIG 4—Method of Attaching Stirrer Cross-piece to Vat, to allow clearance between Vat edge and Cross-piece

A customary plan is to clamp the cross-timber down flush on to the edges of the vat. A system that offers advantages over this, is to insert a hard wood distance piece between each end of the cross-piece and the vat-edges as shown above—thus allowing space for a special vertical sleeve bearing.

For ordinary simple types of stirring gear in *shallow vats*, a foot-step bearing is not necessary for the vertical shaft provided an efficient sleeve-bearing of good length be used In such cases the foot step is an unnecessary complication, but to guard against excessive " lash " or side-swing of the bottom end of the stirrer, a reasonable length of sleeve-bearing must be used A very useful arrangement for a long vertical bearing is shown diagrammatically below.

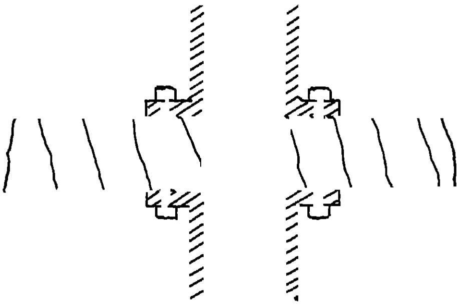


FIG 5.—A useful arrangement for a Long Vertical Bearing, consisting of two Castings used as Top and Bottom Members bolted either side of the Vat Cross-piece

The bottom half of the sleeve-bearing is kept well clear of the contents of the vat by the arrangement of the cross-bearer (as shown in Fig 4) some 6 in. clear of the vat-edge

If it be found necessary to hold down a heavy stirring gear to the vat-top by bolting through the vat-sides, use only brass or gun-metal bolts with "cup-heads" passed through from *inside* the vat, and tightening up from outside Lighter gearings for light duty may be held down with flattened-out straps on the outside of the vat-top, screwed to the vat-side by means of small coach-screws The alternative for very heavy operations where it is deemed inadvisable to pierce the vat, even for brass bolts, is to place a second cross-balk of timber beneath the vat parallel with the gearing cross-piece, the two balks

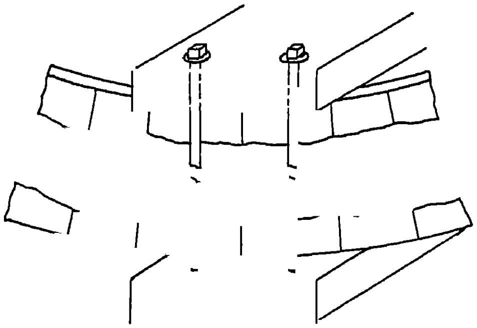


FIG. 6.—Method of Attachment for Heavy Cross Gearing on Large-sized Vats

being drawn together by means of two pairs of long rods, running down the outside of the vat as shown in Fig. 6

This is the method also employed for holding together the sides and base of slate or granite slab tanks and, although unsightly, is reliable.

Baffles, for increasing the efficiency of mixing in a vat, are usually necessary, and generally take the form of longitudinal projections running right down the vat in four or more equidistant positions. If these be in vats of 7-foot diameter or more, the best type for strength, and to save unnecessary boring and bolting, is that in which the baffles form actual narrow staves of the vat (placed edge-on) as shown in drawing No. 7 The only modification that seems desirable in vat beaters of this type is partly to fill in the angles between the vat side and the sides of the beater. This means less local eddy and loss of power (and incidentally less clogging up with colour deposited from the eddies) ; in addition it tends to throw more completely the outer " strata " of the charge towards the centre, and so give a better intermingling of localised portions of the batch

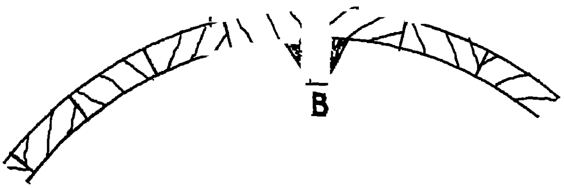


FIG 7.—Section of Vat Illustrating Internal Beater, B, with Angle Fillets Four of these are generally equally spaced round the Vat

For heavy beating up of a charge, as in preparing very insoluble amido bodies for diazotisation, the process may be greatly assisted by beating up the fluid mixture for half an hour, or in some cases an hour or two, in a square section vat, with a cover. This prolonged heavy beating breaks down any big flocculent lumps or small dense nuclei of particles

Among the various patterns of stirring gears in vats, reference may be made to the planetary geared type of waltzing stirrer, which gives very complete mixing, but is only suitable for fairly mobile mixtures and moderate speeds. It is, therefore, very little used in making big batches of pigment colours.

Ordinary practice is to have a central stirrer post moving concentrically in the vat, and this practice is very stereotyped —too stereotyped in fact.

The special type of stirring arrangement which is fully illustrated in drawing No 8 is a far more effective means of rapid and complete intermingling of the whole contents of a large-sized vat. In proportion to the efficiency of the work done, it can be run with less consumption of power and at a lower speed The following is a detailed description, with approximate dimensions and data, of the equipment for a 7-foot diameter vat :—

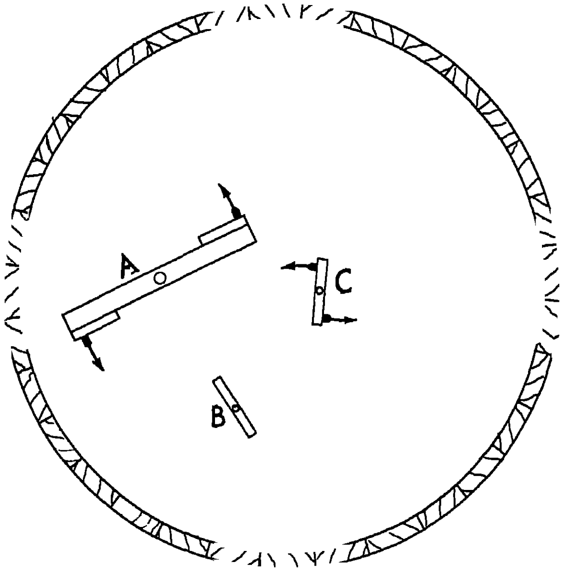


FIG 8 —Ground Plan of Vat with Special Agitation System A, Main Stirrer B, Fixed Deflector Post C, Revolving Partition Post

Taking a diameter across the 7-foot vat, there is fixed at 2 ft. from the edge of the vat a strong vertical stirrer post held at the base in a step-bearing ; this post carries a stirrer, the full depth of the vat and of the design shown in drawing No. 9. This stirrer, complete, is 3 ft. wide, and so sweeps a cylindrical path in the vat, within 6 ins of the vat side, and from the centre of the vat on the other side. Then at a point along the first diameter taken (the line of the stirrer cross-piece actually), 6 in past the centre (or 3 ft. from the opposite side of the vat) is another and lighter vertical " post " which, however, is without stirrer blades and is in the form of a flat bar of pitch-pine, approximately 8 by 2 ins cross section This " stirrer " set 6 in. eccentric is geared to the main stirrer and revolves at, say, 36 r p m to, say, 18 r p.m of the bigger one set nearer the vat edge. This flat strip stirrer is really a partition and guides the whole of the fluid in the vat, in a wide annular path round the vat It is made flat and is rotated by gearing in order to maintain the " cylindrical " sweep of the charge round the vat The actual vat charge moves round

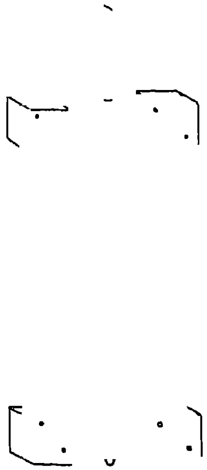


FIG 9—Stirrer Post shown at A in Fig 8

the vat once, when both stirrers are revolving, at perhaps only 10 cycles per minute, but each successive " segment " o fluid comes within the sweep of the bigger stirrer and is completely churned up To give additional efficiency to this type of stirrer, a strong longitudinal deflector board can be fixed firmly to a metal stop in the vat base and solidly attached a the top (to a cross-piece on the vat) to prevent the swir imparted by the main stirrer from going too far This deflecto is shown as " B " in Fig 8

No baffles are needed on the sides of the vat with this type

FOOTSTEP BEARINGS

These are necessary where really heavy work is to be done, and by the use of a suitable type, kept free from dirt and grit, considerable wear and tear of the top bearings and gears will be avoided, as well as saving much power A type which sets up as little friction as any, and is easy to keep clean in use, is the solid block with a hemispherical shaft-housing. These should be bought as matched pairs, i e., " bearer " for vertical shaft or post, and " housing " for the vat base

The two halves of this fitting should be made in acid-resisting metal For the actual adjustment, distinct " play " should be allowed, but it must not be loose, or excessive wear will occur through grit. To fit the footstep to the vat base, it is best to have a strong blank plate bored out symmetrically with the footstep, and the footstep, blank plate and packing are bolted together right through the vat base, with acid-resisting brass or bronze bolts as shown in drawing No. 10. The blank plate (P) should never be omitted, as it saves a lot of strain and possible damage.

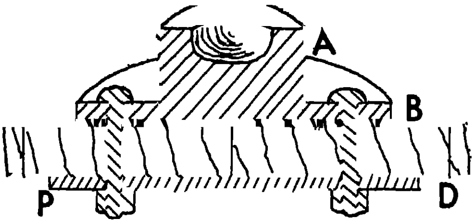


FIG 10—Method of Attachment of Solid Foot Step Bearing for Hemispherical Shaft End
A Acid Resisting Bronze Casting
B Thin Rubber Packing
D Vat Base
P Metal Back Plate

It is necessary to wash out the footstep bearing well with a jet of water between each working batch. Whenever more mobile mixtures are in question, or the stirring required does not involve any heavy strains, then the footstep can be quite well dispensed with, provided the vertical gearing is of ample length , this " suspended " type of stirrer is very simple and gives very little trouble To allow for slight side play, especially on big diameter vats, the bottom stirrer blades should be planed off at an angle as shown in Fig. 11, to allow for proper clearance of the bottom when any side-sway develops.

Footstep bearings should not be used in lead-lined vats if their use can be avoided. If used in lead-lined wood vats they must of course be bolted right through the base of the vat.

A few general observations about vat fittings may be useful here; one very simple precaution which saves considerable time and expense, is to have a " templet " made in tin or sheet iron (with the particulars or reference painted or stamped on) for each individual type of fitment, taking particular care to make the holes symmetrical round a central point and regular. The irregular unsymmetrical boring of holes on fittings is quite a common error and causes much trouble When fitting up a new vat, the " templet " can be carefully checked, and all necessary boring marked out and verified before any actual drilling is done. Strictly speaking there is only one type of bearing for horizontal gearing shafts, in all ordinary work, and that is a good quality ring-oiler bearing with a fair-sized oil-well. This kind of bearing will run for very long periods without much attention, and if covered over with a loose wooden box, as shown in Fig. 12, will be kept quite free from splashings and condensed moisture. Such a cover-box is easily and cheaply made, and should always be used A similar loose cover, of suitable size, should be used where possible over the crown-wheel and pinion.

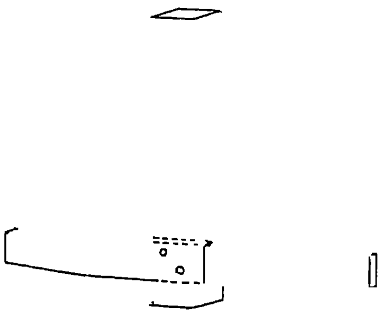


FIG 11—Design of Bottom Blades of Suspended Type of Stirrer

Ordinary plain bushed bearings are not at all desirable for the horizontal shaft of colour vats, as they are too much subjected

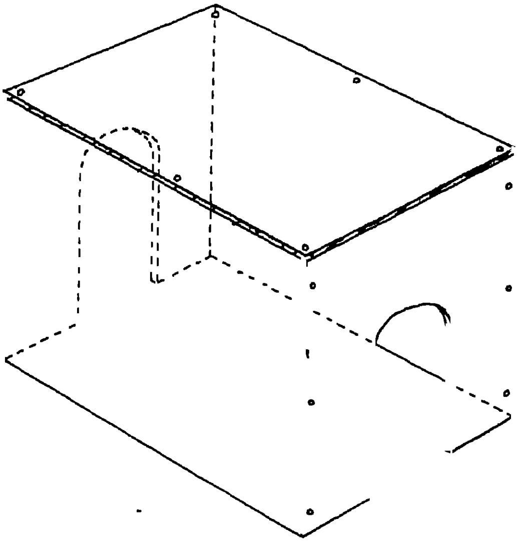


FIG 12 —Loose Wooden Cover Box to place over Horizontal Shaft Bearings on Vats

to heat or moisture (or both) and so require constant re-oiling, a process which is liable to result in dirty oil dripping into the vat. For any special cases where a high speed is required, as in a narrow vat of medium capacity, working on light, fluid material, roller bearings of an enclosed type may be used, but are not usually necessary.

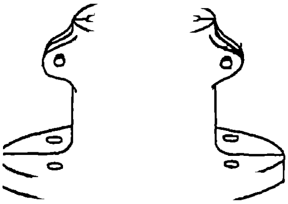


FIG 13 —Upper Member of Double Split Vertical Bearing, showing the Top Member complete, but without Bolts

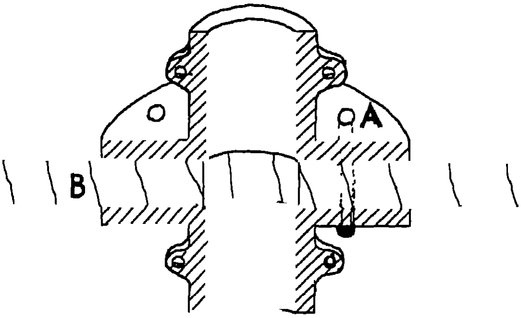


FIG 14 —Two corresponding halves of Split Vertical Bearings as mounted on Stirrer Cross Beam

A Bolt holes through which long bolts pass to draw the two halves together

B Cross Beam of Vat ,to support Stirring Gear

The vertical shaft bearing is one of the most important items of the mechanical fittings on any colour vat, and therefore is given due prominence here A good type of vertical shaft bearing is built up as shown in Figs 13 and 14

The method of fixing this bearing, which permits the quickest change-over or replacement, is to mark out the position of the bolt holes on the top and underside of the cross-timber, and bore right through it When assembling, the bearings are drawn together in position by means of long brass bolts, provided with a hexagon head at one end and threaded at the other. The solid head end of the bolts should be downwards to allow of easy withdrawal, and the bolts must be secured above by lock-nuts In the event of a breakdown, necessitating the removal of the stirrer, or when necessary to replace either of the bearings with a minimum of delay, the bolts can be unscrewed and withdrawn, and the four split halves of the bearings removed, without having to dismantle the crown-wheel. New bearings can then be fitted in a very short time, the worn ones meantime can be re-scraped to a good fit and put ready as spares.

A plain unsplit bearing has, of necessity, to run a good part of its useful life with excessive " play," while the split pattern can be kept in good condition by removing periodically and scraping up to a proper fit.

Proper provision for oil or grease should be made on these vertical bearings before they are assembled, by fitting lubricators on lengths of thin pipe, long enough, and of suitable shape to bring the actual lubricator-cap into an accessible and safe position. These fittings, in common with all screwed, detachable fitments on vats, *should be carefully back-nutted*, to avoid accidental falling off into the vats. The vertical bearings should be made of a good acid-resisting bronze, which will stand up to hard wear.

Even when a cover-box is provided over the gears (see Fig 12) it is best to ensure that no grease or oil can drip from them into the vat; the cover-box will help to lessen this risk, as less oiling will be necessary with a cover in use, a further useful precaution is to nail or screw a small wooden ridge on the cross-piece immediately below the gears, it can be in the form of a tray, and slipped over the vertical shaft before the crown-wheel is fitted.

Another type of gearing used for colour vat stirrers is that in which the vertical shaft, carrying the crown-wheel, is set in a framework which carries a vertical bearing below the crown-wheel and another one at about 2 ft. above, in the top of the framework With this type, fitted in addition with a vertical thrust ball bearing, there is very little need for a footstep bearing

Generally speaking, vertical and horizontal shafts for small vats, relatively shallow, up to 500 gallons capacity, should not be less than 1½ ins. diameter, while all bigger vats up to 2,000 gallons may be of 2 ins, or for heavy work and bigger sizes still, 2½ ins. should be used Whatever arrangements are in use only simple standard sizes should be tolerated—the whole range of vat-fittings can be classified in two or three strengths and dimensions, and thus, by carrying a few spares of each item in each size, defects can at once be remedied and lengthy breakdowns avoided.

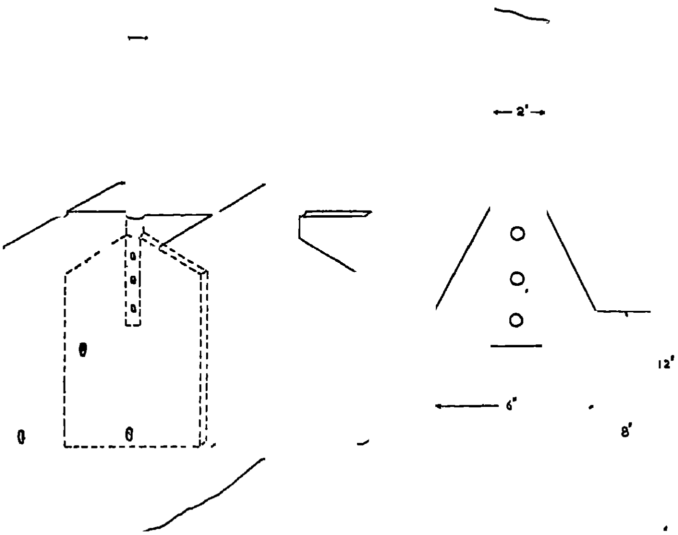


FIG 15—Method of fitting Vertical Wooden Stirrer Post to the Short Steel Spindle

In fitting the vertical wooden stirrer post to the short steel spindle, four points must be aimed at strength, reliability, trueness of fitting, and avoidance of exposed iron fittings. A fairly simple plan, which fulfils these conditions and which can be made standard for any given type of vat, is to fit the lower end of the vertical shaft as shown in Fig 15, with a riveted mild steel plate fitted in a slot in the shaft.

The dimensions of plate shown would suit a 2,000 gallon vat, using an 8-in. square cross-section pitch-pine stirrer post. The steel plate fits fairly tightly in the slotted top of the post, and leaves a narrow slot down each side into which wooden inserts are driven as shewn, thus, the only metal exposed is the nuts of the four brass bolts

Where possible, the stirrer posts should also be interchangeable and only two or three standard sizes used. They would be best bought from a well-equipped timber merchant, who would supply the posts ready slotted and bored to a standard " templet." This can be far better done on a machine, and guaranteed dead true and vertical, than if done by hand in the colour works.

The complete stirrer itself must always be suspended on a vertical thrust ball race, the cost of which is trifling, in comparison with the saving in power and the lessening of wear and tear

A very important point to watch, in fitting up any part of a stirrer, and even more so in attaching fittings to the vat itself, is to bore all necessary holes for plates, bolts, valves, etc, with a good sharp drill-bit of the correct size, so that the bolt or fitting in question is a good fit in the hole ; in the vat itself all large holes especially should be very carefully bored through, till only the point of the bit is through, then bored back carefully from the opposite side. In this way all risk of a splintered and unreliable seating for the attachment is avoided.

In placing the vats in position, the whole of the emplacement must be prepared and levelled up true, ready for the vat, allowing a distinct slope towards the front, so that emptying and washing out may be more complete. A fall of 3 ins from back to front may be allowed in a 6- or 7-foot vat, and 2 ins. in a 4- or 5-foot vat. The actual position of the fittings can best be arranged by inspecting the vat in question prior to its being put in place, and selecting positions for fittings so that all boring and bolting coincides with sound and suitable places in the timbers of the vat When the vat is finally in position, hard wood supports and wedges should be introduced to ensure that the vat is supported evenly at as many points as possible, this will save a lot of distortion and prolong the life, particularly with big heavy sizes.

The base of the vat must be as thick and strong as possible, consistent with economy and reasonable weight, so that foot-step bearings, run-off valves and other fittings can be fitted without any risk of forming weak points in the vat With a good thick base and a flanged run-off neck, the flange of the latter can then be let in flush with the base.

Lead steam pipes for open steam heating in vats should always have the orifice turned away from the side or base of the vat, preferably pointing slightly downwards in the direction of rotation of the stirrer. Careless fitting of an open steam pipe may cause serious local damage to the wood of the vat.

For all purposes where it is necessary to exclude iron, a closed steam coil must be used for boiling up Traces of iron will inevitably be blown through from the steam supply if an open pipe be used.

VALVES

Where possible it is advisable to use valves made of acid-resisting bronze, and for all those cases where they are subjected

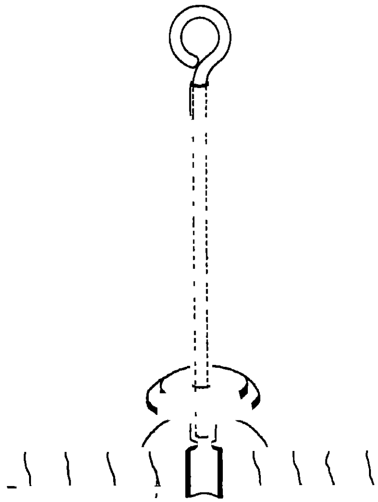


FIG 16.—Plug Rod for Flanged Metal Run-Off in Base of Vat

to excessive abrasion or wear from the working charge, they are easily protected until they are required for running out the charge, by the use of a wooded plug-rod in the inside of the vat This will take the form of a long round pole, turned up conically at one end, to fit in the run-off neck, and then secured in a slot of metal or wood at the top, until it is to be removed for using the valve

The other type, very useful where a flanged metal run-off in the base is used, can be made from a length of iron rod with lead pipe fitted over it and a hard lead flange fitted at the base, faced with a sheet of soft rubber, leaving a short " stem " of the lead-covered iron rod projecting, to keep the rod in place This latter type is shown in Fig. 16.

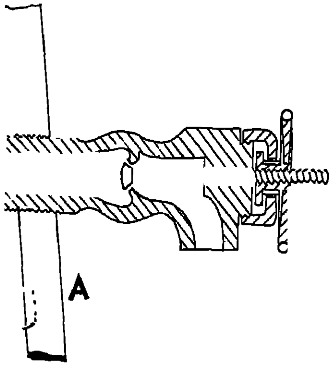


FIG 17—Special Type of Valve for Heavy Colour Work A, is front Side Stave of Vat

For all ordinary valves on colour vats and liquor cisterns, the gland-cock type is rather better as it will keep liquid-tight for a longer period, and any leakage can only occur through the outlet, not from the base of the plug (as does happen with a straight-through plug-cock). Where it is important to stop any slight leakage, then the outlet from the gland-cock can be plugged, or if connected up to a pipe line, a strong canvas and rubber pipe can be interposed, with a wooden screw-clip to close the bore completely.

Valves of the gland and plug types should be kept reconditioned if a lathe is available, not " scrapped " as soon as they leak. The chief wear takes place at the middle section of the plug, and by turning off the bigger diameter ~~left at the~~ widest and narrowest ends of the plug, the valve can then be made a good fit by grinding the plug into its socket with fine emery flour and oil

The more recent types of " lubricated " gland-cocks are very reliable when used for liquids that cause ordinary brass valves to seize-up ; they are made in all kinds of acid-resisting metals, and can be kept constantly lubricated (by a screw-down device) with stiff grease

A type of valve very useful for heavy colour work is shown in Fig 17 , this is useful for running direct into chutes feeding flat box type vacuum filters, as the rate of flow can be very easily regulated while observing the progress of the filter-cake formation. It closes direct on to the seating without any " scoring " action, and the weight of the colour keeps it tight. See Fig. 17.

Power Transmission

Power transmission to colour vat stirrers is seldom done by direct coupling or gears, but may be very efficiently done by silent (Parsons) chain drives for very large vats, or for batteries of vats run from a common shaft, using clutches.

The choice of suitable belting depends largely on the type of work and its situation in the works ; for instance, where heavy and fluctuating loads are met with in a warm, wet atmosphere, the most *reliable* type is solid rubber belting with embedded canvas This kind of belt will give a positive and dependable drive even when wet and fairly slack , it should only be used in thick cross sections, such as 5-ply. Although it may wear out slightly more quickly than a good balata belt of equal weight, it will give more reliable service under the conditions mentioned. No dressing is needed, nor is it permissible, with this type. In a hot, dry atmosphere, for instance near a steam boiler or a drying room, a good chrome leather belt, kept regularly dressed with a little castor oil, will give the longest service, unless the atmosphere be very acid In some cases woven camel-hair belts are good under these conditions, and are often used in colour works

Balata belts of good thickness will give the most economical all-round service where the running conditions are normal They, in common with rubber belts, tend to stretch gradually

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the whole time they are in use, and should be kept reasonably tight by periodical shortening. Dressings should not be used with this type of belt except when absolutely necessary, and then only sparingly.

The only general remarks about the maintenance of belts are that all types should be kept free from grease at all times, and as free from water and moisture as possible. They should be kept at a proper tension and not run over-slack nor excessively tight Whenever fasteners are fitted or replaced, all cutting of belts should be done with the aid of a Tee square and good square joints made carefully by a competent man. This is often regarded too lightly as a trivial job for an odd-man, and slip-shod joints are the result, giving poor transmission and lessening the life of the belt.

Hard, woven-cotton belts are very economical and generally efficient, but should not be used in a place where acid vapours are likely to be present.

PUMPS

It is impossible to work without good efficient pumps, for two main purposes, viz. : (1) pumps for transferring liquids,

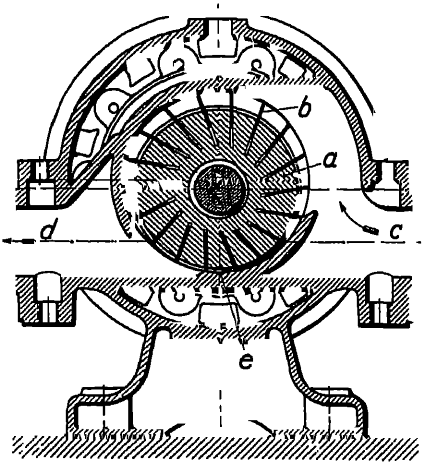

FIG 18 —Special Type of Vacuum Pump without Independent Valves It takes up its own wear by the action of the centrifugally sliding wings, which are shown in the illustration as heavy black radial lines

(*By courtesy of The Rotary Air Compressor Co , Ltd*) and (2) pumps for thick mixtures and sludges. In addition, vacuum pumps will usually be needed for either or both the following processes—firstly, for maintaining a good vacuum in vacuum drying ovens, and secondly, for vacuum filtration with flat, "Nutsch" type, or continuous, cylindrical type Vacuum pumps must be of good make and design, and capable of running for protracted periods, without losing their efficiency. They should not be kept in service once they show bad signs of general wear, nor purchased second-hand.

Pumps with a positive seal and flat disc " floating " valves are the best and give the least trouble

A type of rotary pump with floating blades which automatically adjust themselves to any wear in the casing is shown in Fig. 18 This type has no independent valves or valve chamber

For pumping solutions, wherever possible, a good centrifugal pump is the most reliable and the cheapest The right type for moderate lifts of mobile liquids is one in which a large and substantial packing gland is provided, and in which the blades of the rotor are relatively close together. The average speed for a 2-inch delivery pump of this kind should be 1,100 to 1,200 r p m. A rather different type is necessary for thick mixtures and sludges, namely one in which internal clearances are rather more ample, and with the rotor-blades a little more widely spaced, while the speed of revolution should be about 900 r p m. These modifications allow for the more sluggish movement of the thicker liquids and so specifications for pumps should be made accordingly. These two modifications of a simple and very economical pump should in all cases, for colour work, be made in acid-resisting bronze, or for work with very acid liquids in monel metal, meldrum metal, or similar acid-proof metals. At this point it is well to mention the very useful part played by " Regulus Metal," a hard alloy of antimony and lead This is very useful for run-out plug seatings and other internal fittings for lead-lined vats, and is the best material for valves and centrifugal pumps for sulphuric acid It is strong and rigid and will last many years with reasonable care

The " pumping " of large volumes of weak acid liquors when necessary can be efficiently done with a steam-injector made of regulus metal, so long as the liquid to be pumped is not near the boiling point A special type of air injector which introduces air as well as steam will be found particularly useful for such colours as Prussian blues and Ferrite yellows, requiring the maximum oxidation by air. The general design is illustrated in Fig 19.

In filtering batches of the commoner heavier pigments in a filter-press, a pump will be used with valves. The main points to look for in such a pump are

1. Hard-wearing qualities of the plunger and rings, and of the valves and seatings—in each case resistance to abrasion by the precipitates being filtered is important.

2. Large valves and seatings with good-sized intake and delivery ports

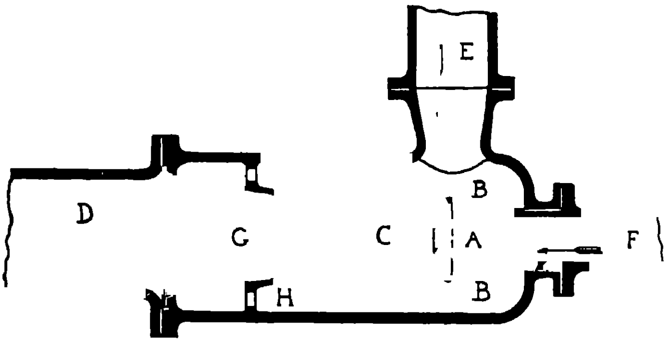

FIG 19 —Simple Type of Injector Pump

It is most desirable to have easily replaceable valves and seatings To increase the efficiency of a filter-press pump, it is better to place in the inlet system, where it will be easily accessible, a non-return valve of ample proportions

A point previously stressed, is that foresight and provision against breakdowns or accidents, so that a minimum of delay is entailed, will save a great deal of time and money In this connection, the provision of one or more efficient portable pumps with strong (embedded) armoured hose suction and delivery pipes should be taken as essential, because in the event of sudden leakage of a vat containing a batch, or in the case of a seized-up valve or outlet, steps can at once be taken to transfer the batch to an empty vat and so save costly material or valuable time

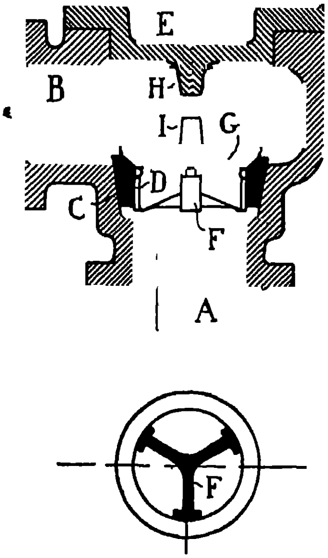

Fig 20a

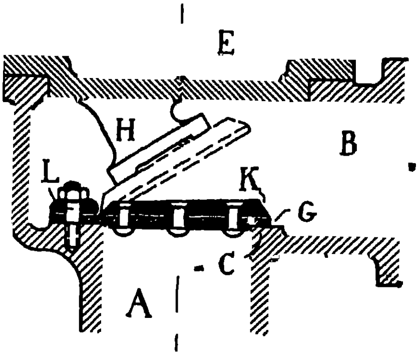

Fig 20b

Types of Valves

a Mitre Valve

b Hinged Clack Valve

c Special Pump with Ball Valves shown at D and C

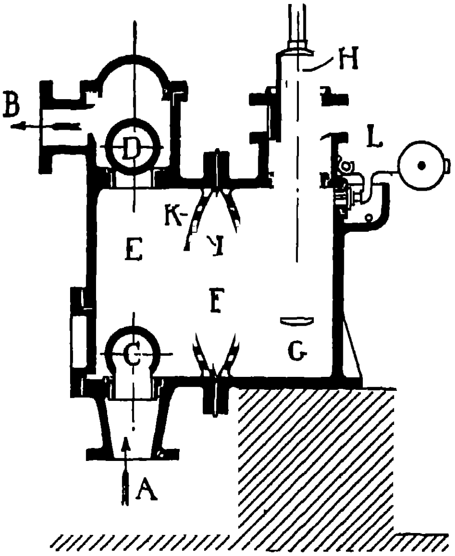

Fig 20c

Type of Valves in Pumps

Three types of useful valves are shown in Figs 20*a*, *b* and *c*.

No. 20*a* is the usual " mitre " valve—which, however, does not resist abrasive wear very well

No 20*b* is a hinged " clack-valve " with a rubber (renewable) flat-facing ; this is a simple reliable type, easily renewed.

No. 20*c* shows (at D and C) " ball-valves " on metal seatings (usually metal balls covered with rubber) They give very free action and long reliable service. This illustration also shows a special type of diaphragm pump. As can be seen from the illustration No 20*c*, this consists of two chambers The left-hand one is furnished with rubber-coated ball-valves and is of acid-proof metal in some cases and vulcanite-lined in others The right-hand chamber is without valves, its only function being to allow the transmission by the plunger " H," moving in plain water, of a reciprocating movement in the fluid to be pumped, as it enters and leaves the left-hand chamber. This action is transmitted by means of the flexible rubber diaphragm " I," which is housed between two concave acid-proof grids " K "

In the case of certain special colours of a soft light texture, approaching a " gelatinous " form—as for example Prussian blues and pure metal salts of dyes of very fine texture—it is necessary to filter by gravitation, using in general a 10 ft. to 15 ft head In this way the cake builds up gradually, and when the most suitable " head " for the colour is discovered, quite good press cakes can be produced. To pump such types into a press is useless, for a hard jelly-like " skin " will form over the cloths, leaving a permanently sloppy or fluid interior to the press cakes. In general it may be said that the rapid pumping to a hard cake of heavy, easily filtered colours and the gravitation feed for light gelatinous colours are two extremes , a commonsense gradation of method between these two will often help materially towards efficiency of the pressing (i.e., both rate of pumping, and pressure should gradually be decreased as the fineness and softness of the colour that is being pressed increases). In this way economy is often effected, even when the press has taken longer to fill, because of the higher solid-content of the resultant cake and the great economy thus effected in drying space and time In the same way, when filtering in an open box type vacuum filter, it often pays to start with a 12 lb. vacuum and increase towards the finish up to 14 lb

FILTRATION PLANT

Filter Presses An efficient large scale works can only afford to use the best and most efficient type of filter-presses, and this means the thorough extraction, washing type in which the cake can be washed with pure water after formation, and subsequently blown with air or steam in order to reduce the water content as far as possible

Vacuum filters are specially useful for handling big quantities of heavy granular colours, such as Chrome yellows and greens or reduced grades of Lithol reds Although the cakes formed from these types of colours are heavy and quite hard, they tend to retain a fair percentage of water, which can be much more efficiently eliminated by any form of vacuum filtration. Efficient washing is rapidly and completely effected on the filter Wooden vacuum filters are to be preferred to iron ones, and are quite essential for most colours. Wood that warps badly with moisture should not be used. Teak or mahogany is very suitable. Pitch-pine may be used, but must be dense and close-grained for this purpose.

Rotary Filters. A more recent type of vacuum filter is that in which the filter cloth is stretched over the periphery of a cylindrical drum, from which the air and filtrate liquids can be continuously evacuated. The pressure of the outer air keeps the facing of filter cloth firmly and evenly pressed on to the perforated outer shell of the drum.

The drum is rotated about a concentric axis and the wet colour "slop" is continuously picked up by suction as the lower face of the drum passes through a trough filled with the colour.

This type of filter works continuously, the thin band of colour paste being constantly removed by a "scraper knife"

In the newer machines provision is made for subjecting the layer of colour to different processes as the drum revolves, for example ·

1st segment	Plain filtration.
2nd segment.	Washing by means of a spray of water directed on to the outside of the drum
3rd segment	Partial drying by drawing air through the layer
4th segment.	Loosening the layer by air pressure from within the drum and finally removing it by means of the scraper

These various functions are carried out simultaneously in the larger size machines by dividing the interior of the drum into segments and providing rotating gland-packed pipe leads for the air, vacuum, wash-water, etc , leads

The pioneer of this type of mill is the well-known " Oliver " rotating filter, which was first produced in America An English mill of similar design is the British " Rovac " filter

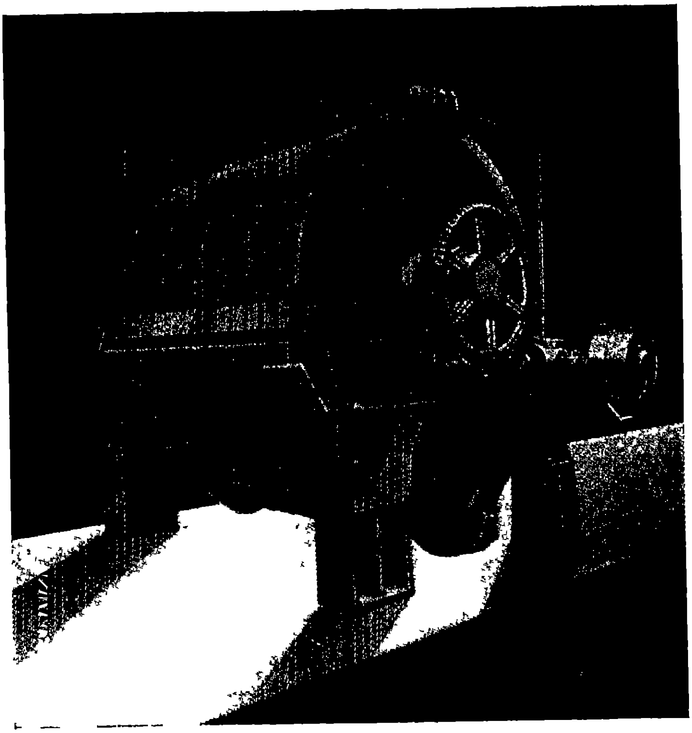

FIG 21—The Rovac Filter Rotary continuous Vacuum Filter showing Drum with Filter Cloth removed

(By courtesy of the Mining and Industrial Equipment Ltd)

The output and efficiency of these filters is very high, and the " cakes " produced are in a thinly laminated form and remarkably free from excess water The drying of the finished pigments is therefore very economical

This type of filter offers many advantages, but is fairly costly to instal. It is very satisfactory for most types of pigments, but when the wet paste colour forms very sticky slimy coatings on the filter cloth, other methods of filtration are to be preferred. For maximum efficiency the pigment should have an " open " or flocculent grain and form hard consistent " cakes " Under these conditions the rotary filter is very simple to use, low in cost of upkeep, and gives a very high output

Where large bulks of soft pulp colours of standard types are regularly produced, and plenty of space is available, it is quite a good plan to instal a number of open box filters, with the interior surface covered with vertical wood laths, and efficient drainage along the base and in the ends, using a strong cotton or linen " bag " of suitable weave as a " liner," to retain the precipitate These cost very little for upkeep or attention and can be used permanently to supplement the output from any other type of press or filter. They are most useful for slow and difficult filtrations, provided space can be allotted to them for a reasonable output. The use of this type will depend on actual trial of the individual colour it is desired to filter in them. When working with a number of them it is often advantageous to bale out the very fluid centre-parts which accumulate overnight and transfer all these to another filter, then, if necessary, transfer all the half-solid pastes to one filter, and thus leave three or four filters again free for a fresh fluid charge

Screw-Presses. In small works or where proper provision for vacuum filtering cannot be provided, hard cakes of colour can be produced by means of a screw-press Pure lead Chrome yellows and greens press up particularly well in this kind of press, and leave cakes with a low moisture content. The screw-press is also useful with some classes of colours, to follow on after ordinary filter-pressing. The soft press cakes are wrapped in cloth bags and pressed in the screw-press. In such cases it is found that the water-content of the cakes can be appreciably lessened A great economy is thus effected in oven space and time of drying A screw-press to be suitable for this work, should be of fairly heavy construction and have a fixed bottom plate and a rising " platten " working between four strong upright pillars set at the corners It must also have a long range of movement to allow a good sized charge, and enough length of screw thread to permit the cakes being sufficiently flattened and compressed The bags of colour are generally separated by strong wooden boards (2-ply, crossed grain) well fastened together by brass screws Thin mild steel plates may be used for any colour where the presence of iron will not spoil the product.

Fig. 22 shows a simple type of screw-press.

Care of Filter Cloths There are two important general points to watch in order to ensure economy and efficiency of filter cloth The cloths on any type of press should always be well wetted and the swelling of the fibres completed before beginning filtration, whether with new or used cloths. In this way, the fine network of fibres and spaces remains stable and holds the colour principally on the outside surface of a continuous finely perforated system. If the filtering be started with dry or only partly wetted cloths, the spaces in the cloth are bigger and allow ingress of fine colour, which is subsequently imprisoned inside the mesh of the cloth, where it becomes fully swollen, and so helps to block the filtering orifices

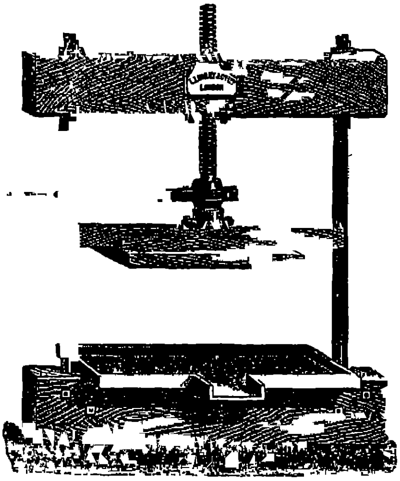

FIG 22—A Simple Type of Screw Press

The life of the cloths is greatly increased by the provision of a really smooth area of flooring on which they can be laid for cleaning by hosing and brushing. Ordinary cement or brick floors very speedily cause abrasion of the cloths, even with normal careful handling.

Another simple precaution, well worth while, is to see that all holes and cut edges of filter-press cloths are cut cleanly and always kept free from loose strands These loose strands get in the way and prevent the proper true facing up of the joints between cloths and frames

REPAIRS AND MAINTENANCE

The maintenance of plant and fittings in good condition and rapid repair in case of break-downs is an important item, if working costs are to be kept low. A pigment colour works has, of necessity, to be run on a considerable scale, and this means a well-equipped fitters' workshop and good men to do the work

Vacuum Plant. Where vacuum plant is in use it is essential to have first-class pipe-screwing tackle, as vacuum pipe work needs very careful and accurate fitting of all screwed work, each threaded piece being made a perfect fit to its actual counterpart. Much of the trouble with vacuum work is due to the ordinary slack threaded joints, made to fit by means of paste compounds, for these joints inevitably break down on vacuum lines and cause trouble

Flanged joints on vacuum plant are desirable where they can be used, and these should present no difficulty, if good quality rubber joints be used.

The doors of vacuum ovens require careful use and attention —the chief points being to see that the rubber sealing-joint round the door, and the flat surface it closes on to, are both kept clean, smooth and level The doors should then be given the minimum amount of tightening-up necessary to ensure an air-tight joint. When the rubber joint, after prolonged use, becomes hard or distorted, it is a great mistake to try to effect an air-tight joint by overstraining the door bolts ; this will often result in the door becoming permanently " sprung " or distorted, thus making it very difficult to guarantee a proper fit, even when new rubber is ultimately fitted As soon as the rubber requires to be replaced, the work should be done by an expert, or at least, by one who has seen the work carried out and understands it. After removing the old rubber, all the old cement at the base of the groove *must* be completely cleaned out and the groove left quite smooth and clean before starting to refit, except in cases where all the old rubber joint peels out, leaving a hard smooth seating of the original cement used, without any breaks. In the latter case it is far better to leave the old cement and brush over evenly with a thin suitable varnish or solution, and fit the new rubber on this facing, with the certainty of having as plane and level a seating as was originally provided

With square doors, where the rubber has to be jointed at the corners, considerable care must be taken to see that the cut end, butting on to the side of the neighbouring piece, is cut absolutely true, square and smooth A small metal guide box to hold the end of the rubber and guide the knife, can easily be made for this purpose

Lathes and Drilling Machines A reliable but simple lathe is very useful for rebushing ordinary types of bearings or glands of pumps, trueing-up valve plugs (as mentioned on page 28) and facing up valves and valve seatings, apart from enabling the fitter to make many small articles which would otherwise be more costly

Even more necessary is a power-driven drilling machine, with a full set of drills for all classes of work This piece of plant will save so much time in drilling flanges, metal straps, supports, etc., in comparison with the small hand power type, that it will pay for itself many times over.

Carpentering The vats, and their careful installation and maintenance, are of such importance that the works carpenter should, if possible, be a man well trained in vat-building and capable of erecting, dismantling, or repairing a vat quickly and reliably.

Electrical Fittings—Illumination Electric light fittings may be a source of trouble, especially when in a very wet steamy atmosphere ; they can, however, be made very reliable if a proper specification be insisted on from the outset All lamp-fittings should be of the totally enclosed type sealed with rubber rings, and having the lead-in wires sealed into the porcelain fittings with some kind of insulating composition Switches also should be of the totally sealed or oil-immersed type. It is also a simple matter to mount all switches and fuses on wax-impregnated wood, carried clear of the walls by porcelain studs ; if this be done they should seldom require attention. If no skilled electrician is employed, hurried temporary repairs only should be carried out by the works fitters, and steps are taken at once to follow this up by a proper and workmanlike repair by skilled electricians.

All switches should be placed where most needed and easily accessible, but at the same time, as far away from hot, wet situations as is consistent with accessibility.

Single wire runs with heavy vulcanised rubber covering are the only reliable kind in bad situations

Hand-lamps with trailing lead-wires should never be used in wet places except for emergency or breakdown work They should be kept in perfect condition and periodically examined —handles kept greased or waxed and everything screwed up tight, above all the flexible leads should be absolutely free from breaks or wear.

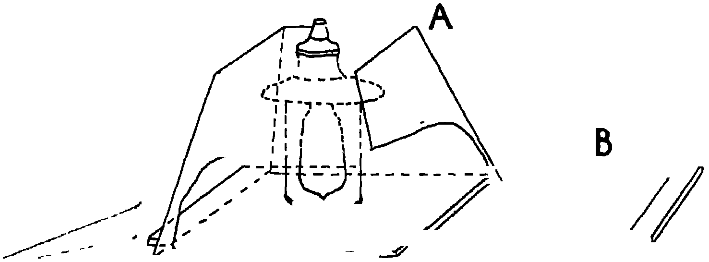

FIG 23 —Enclosed Lamp with movable half-glazed shutter for fitting on the Vat Covers to Illuminate the contents of the Vat

A Damp-Proof Box or Cover for Lamp
B Glass Panel in Wooden Shutter

For illumination inside covered vats, to allow inspection of batches while working, an electric lamp is sometimes fitted *inside* the cover This is a mistake, as it requires endless cleaning and is rather liable to short-circuit. A better plan is shown in Fig 23

It will be seen that this consists of a square conical box on *top* of the cover or lid, the lamp (in a damp-proof fitting) is fitted into the top of this square funnel, slots are left on opposite sides of the funnel near the cover of the vat, while a square hole is cut in the vat cover, corresponding with the mouth of the funnel. Through these slots a light square frame twice the length of the square hole, glazed half-way over with window-glass, is slid. This glass shutter is kept normally closed, and any splashings only coat the wooden half of the slide For batches where practically no splashing occurs, the glass half of the slide may be used, giving continuous illumination of the batch. When heavy splashing is unavoidable, the slide is kept "closed" and only drawn over to the glass side momentarily to allow illumination of the contents of the vat Even when badly splashed, the glass slide is of course much easier to clean than the lamp itself would be.

POWER FOR COLOUR VATS

Electric motors are almost exclusively used for actually driving colour precipitation vats, while steam-driven shafts are employed in other cases where cheap coal is available and heavy continuous work is customary. Either of these sources of power has the advantage of giving full power when any extra load causes a slight slowing up in speed, while steam-driven plant has the big advantage of variable speed. In the case of gas engine driven shafting, and to a lesser extent with A.C electric motors of high frequencies (such as 80 cycles), even a slight slowing up will cause an appreciable falling off in the power just when more is required.

In most pigment works there will be one or more main lines or batteries of big vats for producing the large quantities of staple colours. In any case such an arrangement should be arrived at, and is the only one permitting of economy of skilled labour and supervision, as well as economy in the cost of power. Where a battery of, say, at least six vats can be run in line, an economical and convenient arrangement is to have one common horizontal shaft fitted with clutches to each vat-gearing, and driven by one large motor, through a reducing gear and a Parsons' silent chain of massive proportions. The motor can conveniently be of full capacity to run, say, four of the six vats at full capacity, thus never running all six at once. This means that the work should run out to an average of three vats in constant use, stirring at the same time, driven by a motor capable of properly handling four. In this way the motor can be run most of its time at 75 per cent of full load, which is a good profitable figure for D C, but for A.C. motors as near to 100 per cent as possible gives the maximum efficiency. All six vats can thus be in constant use, arranging them in two groups of three each at different stages of operations, so that when the heaviest stirring on two or three of them is required, the remainder are either being run off, or settling or filtering.

The same general arrangements can be carried out with belt drives, using a very heavy belt for the main drive to a main countershaft and independent belts to each vat, from the countershaft. In this case some economy can be effected by having two stirring speeds, either by means of stepped pulleys or double sets of fast and loose pulleys and two belts to each vat. Generally speaking, very vigorous stirring is needed for all actual mixing and precipitating operations, and these of necessity absorb a lot of power. Other operations requiring lengthy periods of stirring, such as refilling vats with water to wash the colour, and in stirring a finished batch to render it stable and homogeneous, can often be prolonged with advantage for a further period of one or two hours, or even more in some cases. For all these operations, long slow-speed stirring is more suitable and more economical

A main power drive for a battery of vats as just described, should have some provision made for coupling up to an alternative shaft-drive, if there be one available in a suitable position, so that any serious breakdown in the main motor, or transmission, need not necessitate the complete stoppage of all the vats. If this is impossible, the temporary placing of a spare power unit, even if of lower power, but having suitable speed and driving arrangements, should be provided for.

When a countershaft has to be used, it should be of ample size, and with enough bearing points, to ensure freedom from " whip " under heavy loads. For efficiency it is advisable to use ball or roller bearings for this main countershaft. As a general guide for this heavy type of work, a 3-in. countershaft is required for a system needing a 20 to 25 h p. motor, and bearings at not more than 6 ft apart. Wall-boxes are the most rigid fixing for the ends of shaft, where they can be used.

All small independent units of plant, such as plunger pumps for vacuum or for presswork, can generally be run most economically as a combined steam engine and pump unit, steam always being available in the pigment colour works The cost of upkeep of small electric motors in such cases, and their liability to be affected by moisture, to some extent rules them out, and the great advantage of wide variation of speed with the direct steam-driven unit is of the utmost importance, and in fact is almost an essential factor for filter-pressing.

Motors and Switch Gear. The installation of motors and switch-gear requires special care in a pigment colour works owing to the unfavourable conditions usually existing Both motors and switches should be of damp-proof, totally enclosed types for all damp situations, and motors should always be mounted well clear of the floor, either on wall brackets or on substantial pillars or bed plates. For prolonged heavy work it may be advisable to instal a special motor with ventilating ducts for air-cooling. Another special precaution, that will always be necessary, is to see that any motor used for circulating air in drying ovens is given a suitable emplacement. Two arrangements are equally satisfactory (1) To place the motor on a floor level above or below the drying rooms, or adjoining them, and drive through a gap sufficient for the free play of the belt (2) To keep the motor reasonably cool on protracted runs by mounting a self-ventilating motor in a box close to an outer wall, and arranging ventilation ducts from the box to the outer air

Where the outlay permits the replacement of an existing electro-motor fan system or in planning for a new unit, there seems to be only one really sound method of driving a drying oven ventilating fan for reliability over long periods, cheapness of upkeep and efficiency—that is the high speed, direct coupled, steam-engine fan unit, as shown in Fig 24.

This type, if run with steam at a fair pressure can be made very economical by utilising the exhaust steam as an air heater, and if not sufficient for a main heater the steam will heat an auxiliary heater and so allow of a smaller main heater.

PULLEYS

Wooden pulleys are not really advisable in a pigment colour works, except for fairly light duty and under good working conditions For all work requiring heavy and reliable drives, split iron pulleys keyed to the shaft are necessary In the case of fast and loose drives, both the wide driving pulley and the fast and loose driven pulleys will of course have flat faces Where a fixed drive is in use, without fast and loose pulleys, a crowned face will give more certain alignment and a more efficient drive.

DRYING SYSTEMS

Without some efficient provision for keeping cool the motor driving the fan for the drying ovens, considerable trouble and expense are certain Probably the soundest method of all is that advocated by most of the well-known heating and ventilating engineering firms, and shown in Fig 24, namely, a direct coupled fan with a high-speed steam engine in one unit, which utilises the exhaust steam from the engine to heat either the main heater, or at least an auxiliary heater for the hot-air system

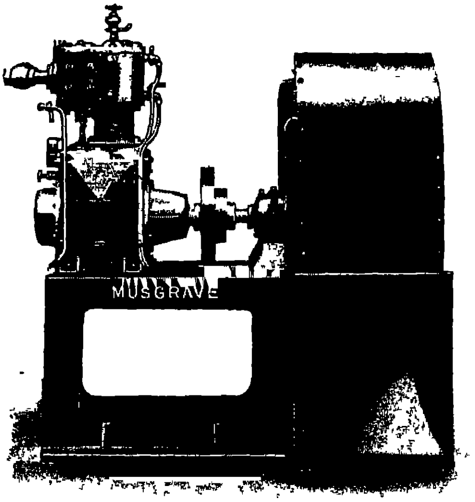

FIG 24 —Direct Coupled Ventilating Fan and Exhaust Steam Driving Engine

(By courtesy of Musgrave & Co , Ltd)

The question of efficient drying is a highly specialised business, and much depends on the proper position and proportion of all ducts and spaces throughout the system, on the most efficient humidity figure being maintained, and the rate of flow and temperature of the hot-air current, as well as its rate of gradual replacement by fresh air Reliable data for most of these problems can be obtained from the heating and ventilating plant manufacturers, and it will usually pay to follow their advice in all the main aspects and only to " experiment " very cautiously with improvements when everything is running properly.

The actual drying plant and its installation is beyond the scope of this book, but the general precautions necessary may be mentioned , they include, in order of their importance

1. Proper supervision of all goods going into the ovens, to make quite sure that any particular type of colour is passed into the ovens with the maximum of solid content , this effects much economy both by increasing the actual weight of colour in a charge and decreasing the amount of water to be eliminated This stage of the work should include proper care to see that all trays are as equally loaded as possible, and above all not overloaded, and that the material has been well subdivided

2. The careful regulation of the air pressure (rate of flow), temperature, and humidity (at certain definite points) to as nearly as possible the figures recommended by the designers of the plant, or to those found best by actual experiments with the plant.

3 Periodical examination to ensure freedom from leaks in the steam-heating system. This is quite important, as a small leak may greatly add to the time and cost of drying a charge.

4 Regular and thorough breaking up of the material on the trays during the later stages of drying will greatly add to the efficiency of the plant, especially with colours which do not leave a very porous, open-grained mass on drying. In doing this, it is of course customary to change the positions of trays in order to counteract as far as possible differences in the drying efficiency of various positions in the oven. If very rapid drying takes place in the oven section nearest to the main inlet for hot air, and rather too slow drying in the sections further away, it is sometimes well to modify the shape and size of the trays and their edges in this first oven, to allow more of the fresh, hot air to be deflected round them, and distributed more evenly in the succeeding sections of the oven If it should be necessary to deal with any wet colour or paste which normally may evolve, even traces, or an appreciable quantity of acetic acid or hydrochloric acid, this material should be dried in a special plant which is acid-proof, otherwise much damage may be done If it be necessary to deal with a small plant of this

kind, or, for instance, to draw unpleasant acid vapours from a making-vat, and the process does not warrant the expense of a fan in ceramic, or in acid-proof alloy, then good service can be obtained from a simple heavy type of cast-iron cased fan.

The drying of wet pigment on racks in hot-rooms over the steam boilers, or in rooms fitted with steam or hot water pipes, but in which there is no system of hot-air circulation, should be carried out with attention to two factors—(1) the colour should be very evenly spread and well broken up, and (2) the trays should not be overloaded. In addition, the turning over and breaking up of the cakes should be more thorough than in ovens with hot-air circulation.

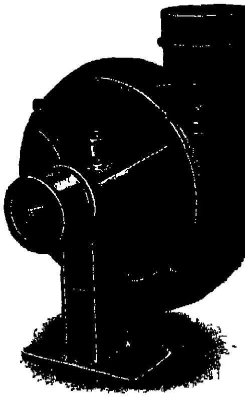

FIG 25—Cast Iron Cased Fan for Acid Vapours

(*By courtesy of Musgrave & Co, Ltd*)

Vacuum Ovens Vacuum ovens require special attention and some points have already been mentioned on page (39) It is imperative to maintain the vacuum in the oven, throughout the run, above the minimum stated by the makers, or the drying operation will prove costly This involves great care and efficiency in the use and maintenance of this section of plant. In addition the temperature must be kept well up to the figure decided on for the colour to be dried

The condenser must be kept well sealed and working at full efficiency. Connecting pipes from oven to condenser should of course slope down towards the condenser and be well lagged to avoid condensed water running back into the oven.

A faulty condenser will cause the time of drying to be greatly increased or even stop the drying entirely. Finally the pump must be kept in perfect condition and should be of similar design to those already mentioned, or of the special type shown in Fig. 20c, and have either an oil or water seal.

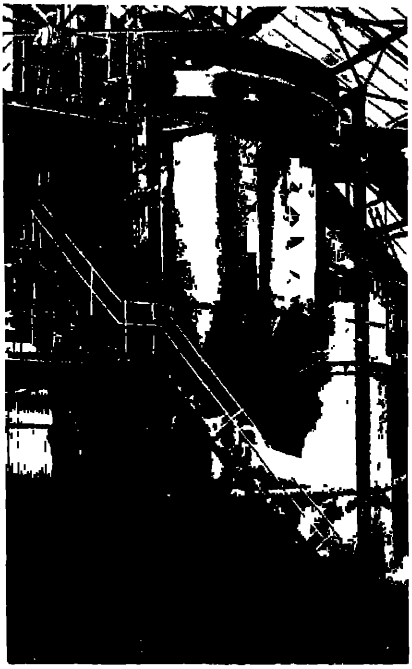

FIG 26.—The Kestner Spray Dryer

The trays in this type of oven can be much more heavily loaded than in the ordinary type and the colour will require no attention till quite dry. A heavy charge can be efficiently dried, provided the temperature be high enough and the condenser working at full efficiency. Under such circumstances a good vacuum oven will, with care, give a lower drying cost per ton of colour than any ordinary type working at atmospheric pressure

Other types of drying plant, such as revolving dryers and the newer type which injects the fluid colour mixture into a large heated expansion chamber by means of a jet of superheated steam, are not met with in the average pigment works, but the latter type after full practical trial will probably supersede some of the older and less economical types. Such drying plants could only be installed by a large scale manufacturer, for they will only give full efficiency when worked on continuous runs , they must of necessity be made in fairly large sizes, and are not so quickly changed over from one type of colour to another , the working conditions (actual temperature, jet pressure, and rate of flow, etc) need careful and individual attention for different types of colours These spray or jet dryers have unique advantages in dealing with very large continuous outputs and give fine light powders of uniform dryness and texture

While such a type does not seem, at the present time, within the scope of the small manufacturer making a wide range of fine colours, on the other hand the vacuum oven, with its cleanliness, low temperature, high drying efficiency, and rapid output with small floor space, should be considered as an indispensable part of the colour works drying equipment.

A comprehensive series of interesting papers has recently been given before the Institution of Chemical Engineers (Dec. 6 and 7, 1928) during this society's " Conference on Drying " A study of these papers (reported in brief in " The Industrial Chemist," Dec. 1928 and Jan. 1929) will be found very profitable.

GRINDING PLANT AND METHODS

The uniform, correct texture and fineness of the final products is most important, from the user's point of view, whether the colours be made in the dry colour section of a large paint works, or made by a pigment manufacturer for sale to other users. Above all, uniformity of *average fineness* of particle and of particle shape and character, should be aimed at In using the expression " average fineness " it is intended to call attention to the fact that, while very fine grinding is necessary in most cases, an average of well-assorted finenesses is necessary for the best results in paint work The subject of fineness of particles is dealt with in Chap VII. Once the consumer has been supplied with a material, the physical properties of which suit his requirements, any variation in these particulars will cause trouble and dissatisfaction. These variations may exist independently of shade and strength, although any great variation in particle size or shape will usually be reflected in a considerable change in strength, and in the shade of the undertone.

The type and extent of the grinding installation will depend on the output of properly dried material from the complete drying plant, and the amount and kind of the various colours to be ground. It is necessary to have careful and continuous supervision of all drying arrangements, to ensure that heat and oven space is not wastefully occupied by material which is fully dried ; on the other hand, to grind any of the colour before it is thoroughly dry will prolong the grinding and, in most cases, spoil the texture and fineness of the powder.

When feeding roughly powdered colour into "Kek" or "Raymond" mills, and similar types, a screen should be used to remove particles of wood, etc , and a magnet to ensure that no nails or particles of iron pass into the mill.

When grinding a wide range of fine colours in moderate quantities the chief requirements are a fine soft product, rapid change-over from one colour to another, and clean bright products. In this case mills of the "Kek" type will give the best service.

For handling large outputs of heavy and coarser types of colours, such as reduced Brunswick greens and cheap fast reds, where a large percentage of barytes may be present, a heavy double roller pan mill will give economical and reliable service. Brunswick greens, Lithol reds, and reduced celestial blues in big quantities are best ground in this type of mill, which indeed is essential for "developing" some shades and if ground to the right degree the pigment will have a bright rich appearance in the dry state, which is an advantage from the selling point of view. On the Continent, the use of medium-sized two-roller pan mills, usually arranged in batteries, seems to be in great favour. Each mill is reserved for continuous runs on one pigment, and no doubt where floor space is available and the mills are kept on constant output of one material, this system gives a very standard product at a low cost of upkeep. For this kind of work the mills are totally enclosed with loose covers fitted with balance weights to enable them to be raised easily, and are connected to a suction plant for carrying off dust

The pattern having moving rollers and a fixed pan tends to clog with some colours and the rollers have a tendency to "ride" over the colour For this reason, the other type, having a revolving pan, is to be greatly preferred, and gives much more positive "feed" under the rollers and rather more shearing of the particles

Where really large outputs of very finely ground material are required, the well-known "Raymond" mill is the only economical proposition Although its initial cost, its installation and upkeep are all high, its enormous output compared with the older types, and its automatic grading of the fineness of the product, enable this mill easily to hold its own where large and regular output is required Its great efficiency is dependent on two factors—(1) the high speed, which ensures a perfect shearing of the particles, and (2) its air-separation of ground and unground material, which prevents the "cushioning" of coarse particles with already ground finer stuffs and constantly returns the coarse particles to the area where the grinding is heaviest

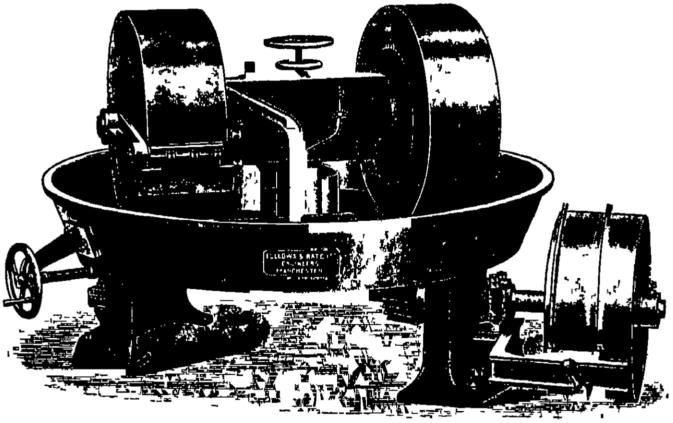

Fig 27 —Pan Type of Grinder
(*By courtesy of Follows & Bate, Ltd*)

The "Raymond" being a costly machine and designed on scientific lines requires, of course, skilled handling and careful maintenance to keep operating costs down and to avoid breakdowns or inefficient running These remarks apply of course to all the other types of grinding machines, but the necessity is not perhaps so noticeable with a much cheaper type of machine. In all types of grinding mill the maximum efficiency is only obtained within comparatively narrow limits of rate of feed in the case of continuous operating types, or of bulk of charge in the case of the intermittent types

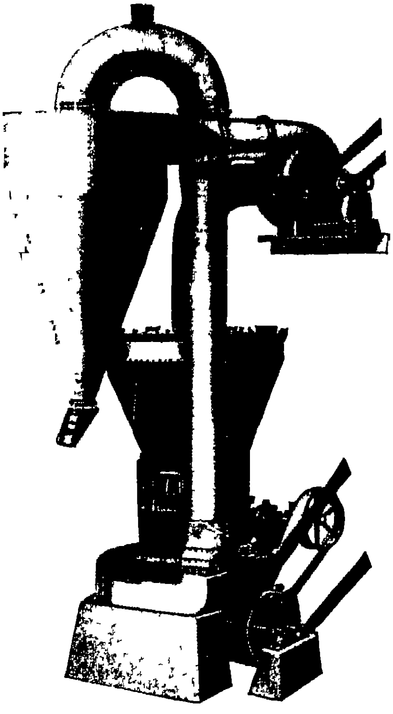

Fig 28 —The Raymond Mill
(By courtesy of the Mining and Industrial Equipment Ltd)

There is one efficient rate of charge for any given colour to a required fineness, and to feed either much slower or much faster will only result in a loss of efficiency If the grinding operations be in the charge of an intelligent and experienced man he will acquire experience with his own plant, working on his own firm's products, and obtain very efficient working on each different type , when this result is attained with any particular colour the exact method of drying and grinding must be adhered to as rigidly as possible in every detail.

DRY GRINDING MILLS

(1) *The Pan Mill* The pan mill offers particular advantages for grinding and developing such colours as reduced strengths of .

Lithol Reds
Permanent Reds B, 2B, etc
Helio Red R L
Brunswick Greens and Blues
Chrome Yellows.

and generally speaking, any colours which are blended or reduced in the dry state.

The pan mill or edge-runner is particularly useful for grinding, where incorporating of other colours or a fair amount of tinting up to exact shade has to be done In these cases, a complete mixed charge, or the main colour with the addition of approximately all the calculated " shading " additions, can be run in one operation If the scrapers have been suitably set to give a rapid and complete turning over of the particular charge in the mill (the setting should vary as between heavy inert charges and lighter fluffier material), then a perfectly homogeneous mixture is quickly obtained In making combined shades such as violets or purples from fast bluish reds and ultra blues, or greens from Celestial or Chinese blues with zinc or lead chromate, or with pure Pigment Yellows, then the pan mill will usually give bright rich powders, well incorporated, and of good selling appearance. A good practice is to " finish " these on a " Kek " mill

Bright fine colours for lithographic work or those that are liable to discolour if ground in iron mills can be ground in pan mills which have granite or porphyry rollers and pan-bottoms

This type of mill can be used for the manufacture of oxychloride of lead, from litharge and salt, as a finely ground, uniform paste, where an iron pan mill on the same work would quickly show heavy corrosion, but as already mentioned, wooden ball-mills with stone balls are used in some cases, such as for " reflex " lakes

The pan mill is above all useful for the important range of insoluble pigment colours, usually bought in paste form and requiring only thorough incorporation with a suitable base drying and grinding (Several useful hints are given on this subject in Chap. XIII, pages 170-176)

(2) *The "Kek" Mill* The "Kek" mill is very efficient and takes up small floor-space, while the wearing parts are easily replaced. For all types of colours requiring a straight simple grinding to a fine light powder, and not requiring any tinting up or mixing, the "Kek" mill is most generally used

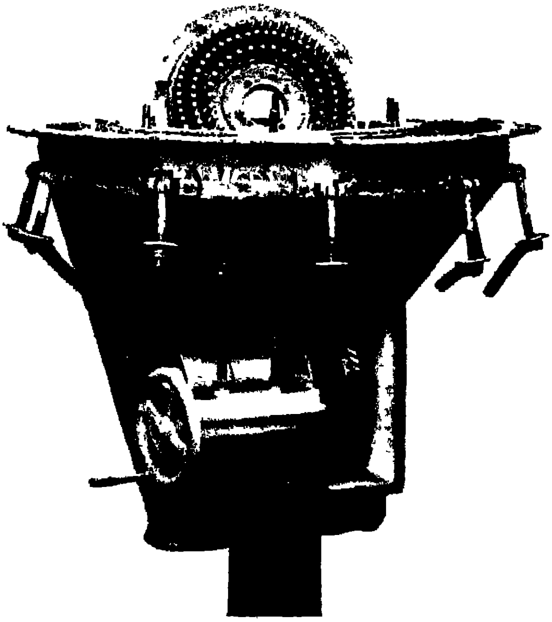

FIG 29 —Kek Mill (No 4 size) with Oil Bath Door removed to show Driving Gear, and with Top Disc lifted

(By courtesy of The Buffoline Noiseless Gear Co , Ltd)

Such colours as the following are usually ground in this type of machine

Prussian and Chinese blues.
Pure Chromate-Prussian greens.
Most pure lake colours

Some colours are obtainable at their best and brightest only when ground with a high-speed shearing action, without heavy crushing pressure. Such colours are best ground in a "Kek" mill

(3) *Ball Mills* Most fine colours made for printing inks are of very soft texture, even before grinding, and generally require to be only lightly powdered in ball mills and *not* reduced to a very fine light powder. A fine fluffy powder does not readily incorporate with the "Litho" oil or varnish, while a coarser (but soft) powder will do so The "reflex" colours, which owe their special property to the fact that they consist of minute crystals, must not be subjected to a crushing action, as they would lose part of their special characteristic appearance. They are therefore invariably powdered in a ball mill.

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SECTION 2

ANALYTICAL AND TESTING SECTION

CHAPTER IV

LABORATORY EQUIPMENT AND WORKS CONTROL

THE WORKS LABORATORY

THE laboratory for the control of pigment colour works processes, for the proper testing and matching of samples received, and for the examination and passing of all finished products, must be well equipped, of ample size, and be provided with good natural and artificial lighting. The actual scope and size of operations will influence to some extent the size and the details of the equipment. On the other hand, however small the laboratory may be, it should be well equipped and well lighted, and restricted as little as possible in the range of work that can be done. Apart from the lighting and usual equipment, the special requirements are

1 A good microscope with objectives and eyepieces for magnifications of about 80 diameters, and others for magnifications of about 400 to 600 diameters.

2. One piece of apparatus not included among essential items, because it often appears to be looked upon as an unnecessary luxury in a pigment colour laboratory, is a simple form of spectroscope Actually the author considers this a most valuable and almost essential instrument for such a laboratory, especially where madder lakes are dealt with to any extent, or other work necessitating the rapid detection of traces of metals, such as calcium, tin, chromium, etc.

The shades of these pigments largely depend on traces of various metals present, and the initial cost of a spectroscope, which with practice will make the detection of such traces much more rapid and certain, will soon be justified when compared with the lengthy process of group analysis and its uncertainty in recognising traces of calcium, magnesium, tin, etc.

3. A reliable source of power with a shafting running the full length of at least one bench This should be a light but substantial equipment, capable of running daily for long periods without trouble, so that all experimental colour trials

can be made with mechanical stirring and a number of tests conducted simultaneously if necessary

4 All main work benches lead-lined and having a raised border, with at least one large sink fitted flush in each bench. This is the best system owing to the wet and splashing type of work carried out. Adequate waste-pipes and traps should be fitted to all such sinks

5 Where possible, at least at one point in the laboratory, a supply of works steam and also of air under pressure. In some laboratories vacuum is also laid on, but in a small establishment this seems to be an unnecessary fitment, in view of the reliability and efficiency of vacuum pumps of the injector type operated by tap water

6 A well-lighted bench, preferably in teak, and lighted by an unobstructed north light, for palette and colour-matching work. Much time and uncertainty can be avoided by having a suitable bench for this work, properly lighted.

7 A fading-test apparatus for accelerated comparative tests. Either a K B B. lamp (or a Cooper Hewitt mercury-vapour lamp for quick results), or a Fadeometer.

8 Finally, a good expanse of window space glazed with "Vita" glass and with frames to fit, for keeping a regular series of actual daylight tests of standard products under exposure. This will preferably be away from the laboratory, or any other fume-laden atmosphere

The two items for fading tests have been placed last, not as being by any means of least importance, but because they naturally come at the end of operations as the final test This part of the equipment and work is actually of paramount importance

If in addition the enterprise is big enough to permit of the use of a scientific colour-matching instrument, then the general trend of official opinion should be followed in the choice of a suitable type, so that any subsequent classification of products may be the more likely to coincide with that of official bodies and physicists The instrument that appears to hold this official approval is the "Guild Trichromatic Colorimeter."

In establishing any matching scheme or nomenclature by such means, it must be remembered that all types of surface will reflect a certain proportion of unaltered light, thus "diluting" the shade itself with extra white light This ffect may give quite misleading matchings unless great are be taken to standardise and stabilise the type of urface to be viewed. This point was mentioned by . Guild during a discussion on "Colour Standardisation nd Testing," before the Oil and Colour Chemists' Associaion (see the Journal of the Society, Vol XI, No. 102 Dec 8, 922, page 392) Guild suggested a very thin coating of beeswax as one likely method of retaining a standard urface, where flat surfaces are to be compared with glossy or emi-glossy patterns

These items constitute the main essentials for the fitting up of the laboratory itself. In addition, one or two ordinary chemical balances should be used for general weighings and matchings, the fine balance being kept of course for analytical work.

General Apparatus. Ordinary glass beakers, if used for general mixing and colour washing work, can become an expensive item, straight sided glazed earthenware jars are very useful and cheap for mixing, washing and testing small colour batches in the cold. Otherwise, for cold work, heavy glass beakers should be used; for boiling up work, porcelain or Pyrex beakers are the cheapest in the end. Enamelled iron or steel vessels are not at all satisfactory for boiling up work in the laboratory

Other items of ordinary replaceable apparatus which should be abundantly supplied and kept fitted up ready for use, are filter flasks and funnels. There should never be any delay in waiting for these if a number of tests have to be done. The very small sizes are not particularly useful for quick routine colour work, and a good-sized funnel should be used, giving a thin hard layer of paste colour for drying off rapidly. Filter flasks are best arranged so that several are connected to the pump through a large stoneware or glass receiver. A tap is fitted to each connection and to the branch from the pump. When a high vacuum is obtained the pump connection is closed and the water turned off.

A set of standard thermometers should be kept, so that all the thermometers in the works can be checked comparatively This is most important and should be regularly done about once a month.

Organisation. The actual routine work of the laboratory should be as definitely subdivided as possible. Many of the vitally important characteristics of pigments are not chemical, but purely physical, and a technical man familiar with a certain range of the colours, and dealing with a definite series of tests, will naturally be quicker to observe any departure from the normal.

For instance, one skilled technical man and an assistant can deal with all the laboratory tests of solutions, colour batch end-point or coupling tests, run-off liquors, etc In the case of a works producing large quantities of Alizarin lakes one man should concentrate on supervising everything connected with this range of pigments

Most of the colour matching should be done by one man or group of men This work includes examining dry colour samples received for matching, testing out batches ready for grinding, and calculating quantities for shading or mixing with works batches, and finally checking all finished dry colour against the respective standards.

TESTING MATERIALS

Use of the Microscope. The fullest use should be made of the microscope for examination of the fineness and form of all bases used in the works, and of all finished products, and also to examine samples which have to be matched. In making examination of competitive samples with a good microscope, the type of base can often be detected at once and any shading up with small percentages of tinting colours, or any admixture of two pigments to obtain the given colour, are at once detected with certainty. In examining Chrome or reduced Brunswick greens, it can also be seen at once whether they have been made by a wet precipitation process or whether they are mixtures combined in a pan mill.

A further field of utility for a good microscope is in " micro " analysis as described by H Green in five articles appearing in " The Paint, Oil and Chemical Review " (March, April, May, June and July, 1927). This needs a good microscope equipped with a 2 mm. objective and a 15 X eyepiece, and at this magnification (about 1,000 diameters) a number of " micro " reactions may be performed on the prepared film of pigment and the effect of the reagents observed *on the various individual primary particles.* Article No. 3 of this series (May 26th, 1927, page 10) is of the greatest use and interest to the pigment chemist It deals with such subjects as the determination of the origin and type of small percentages of zinc (as to whether it be present in the form of zinc oxide, zinc sulphide, or as lithopone), small percentages of lead (as to whether present as basic sulphate, or as white lead), and whether zinc with a small percentage of lead is a leaded, sublimed product, or a zinc oxide with added lead It also gives very useful information about the differentiation between types of blacks present in even pale grey shades Once a certain amount of practice has been acquired in this kind of work, the chemist's own ingenuity will suggest and find many other real time-saving ways of doing work accurately with the microscope.

In all cases, when examining samples of unknown composition, a few simple chemical tests will be advisable as a beginning, in order to obtain a general idea of the composition of the base and of the pigment The microscope will then often prove a quick means of further classifying or confirming the actual type of base and composition of pigment

Analysis of Lake Colours For a full and systematic analysis of an organic pigment of unknown composition, the detailed scheme described in the special analytical table drawn up by Professor A. G Green (which is given in full detail in the Journal of the Oil and Colour Chemists' Association, No 92, Vol XI , pages 38 to 48 inclusive) is a very valuable help, and gives definite, consistent results in most cases, but is liable to fail with a few mixed pigments

Inorganic Colours A full and more definite analytical scheme for all classes of inorganic substrata and pigments is clearly and fully set out in " The Analysis of Pigments, Paints and Varnishes," by J. J. Fox, F I C, and T. H Bowles. This work gives a complete and reliable scheme for accurate and detailed analysis.

Pigments in Oil Analysis of submitted samples may often involve the analysis of a pigment ground in oil, or in a ready-mixed oil or varnish paint. In the case of heavy pigments which are not superfinely ground, pigments can often be best separated from oil by gradually mixing a weighed sample with about twice its own weight of pure turpentine till quite free from lumps and pasty particles, and then filling up in a tall narrow beaker with about 20 times the bulk of *ether*. The whole mixture should be well stirred on a hot plate or in a bath of hot water and then allowed to settle The main separation is effected by decantation and the treatment repeated Finally the pigment is washed through a fine gauze (about 100 mesh, not finer), with clean ether, to retain any jelly-like bits of skin or gum which may be present The pigment after draining on a filter will be sufficiently free from oil and varnish to be quite satisfactory for analysis The only other certain way of separation, and more particularly applicable to lighter and ultra finely ground paints of the enamel type, is a fairly long run in a small laboratory super-centrifuge , one running at not less than 10,000 to 12,000 revolutions per minute is necessary for a proper separation ; the ordinary hand power type running at only 4,000 to 6,000 revolutions per minute being useless for finely ground enamels made up of light pigments In separating by super-centrifuging, a second "run" with fresh ether will be necessary if the pigment is required well freed from oil and varnish , in this type of separation, the small amount of turpentine for the first breaking down of the paint, the subsequent warming, and the washing through a gauze to eliminate solid particles of skin or gum, are all a great assistance

To facilitate separation, a big bulk of the lower gravity solvent is needed in proportion to the heavier gravity vehicle contained in the paint, so that the final mixture of fluids is as mobile and light as possible, thus permitting of quicker separation of the solids.

Petroleum ether should not be used for the general range of these separations because when such separations are done in the cold, or become cold in the process of separation, most of the metallic soaps of various kinds, always present in small quantity (even in most paste colours ground in pure linseed oil), will separate and leave a greasy pigment for the final analysis When good clean "methylated" ether is used, and the extraction done by warming, these traces of soaps, once in solution, remain dissolved

When dealing with varnish paints and enamels, extraction by means of petroleum ether is even more undesirable, for although the whole of any fossil-gum varnish or lime resinate present may dissolve quite well, and even remain dissolved in a *small* added quantity of petroleum ether, when a sufficiently large bulk is added to allow of proper separation and washing, such constituents as Congo gums, hardened rosin, and to a lesser degree Manila gums, will separate to an appreciable extent on standing. In the *rare* cases where Pontianac gums are present in an enamel paint varnish, these will be found to be almost insoluble in excess of cold petroleum ether

In a laboratory where many samples of paints have to be separated for examination of the pigment or the vehicle, and a large quantity of ether has to be used in consequence, care should be taken to have an efficient distillation apparatus with a good type of condenser kept for the purpose of recovering all the ether used. Such work can only be done safely on a steam-heated water bath

The only alternative method of separation, which is rather simpler, but does not always succeed, is to grind up well a prearranged weight of (*a*) very finely ground mineral barytes or (*b*) very finely ground silica flour, with some of the paint

If, say, 2 grammes of the paint be taken and either 10 or 20 grammes of (*a*) or (*b*) and the whole well puddled up in a glass mortar with turpentine, about 10 c c , then on washing into a tall beaker with ether, warming, and well stirring, very often the one or the other will succeed in carrying down practically all the finest of the pigment. The silica is to be preferred as it still permits of accurate estimation of barytes, five times the weight of the paint should be used rather than ten times, if it will do the work Of course, all the precipitate must be recovered and weighed, and so the proportion of silica to original pigment can be known and an allowance made

As the matching of customers' or competitors' samples is so frequently necessary and is usually rather urgent, it is well to have a properly organised method of dealing with these. One man should be responsible for all such samples received, first entering them in a "sample-book," with full particulars, then painting a reference number on the tin or box to ensure its not being lost or mistaken for any other sample The sample should next be given a rapid general examination for shade, strength and undertone As soon as that is completed and the assumed nearest type to it has been decided on from the stock colours, then very weak reduced shades in white lead, approximately 25 to 1 for a weak colour and 50 to 1 for a very strong colour should be painted on tin in quick varnish and turpentine (preferably with a half matte finish), for fading test A solution at 20 per cent strength of damar gum in pure turpentine, with a little strong boiled oil, makes a very suitable quick binder, quite pale in colour, and with no action on most types of pigment. One standard mixture should be used and adhered to, 20 parts damar gum, melted at 200° C. with 10 parts boiled oil, then cooled to 150° C. and "thinned" with 70 parts of pure turpentine, is a very suitable thin varnish The tests should be ground out on the palette, adjusting the shade of the sample and the assumed similar stock type to the same depth As soon as possible these tests should be put under an accelerated fading test, especially if the sample has been proved, or is assumed, to be an organic pigment lake In this latter case, some knowledge of the fastness to light may greatly facilitate a decision as to its type or the selection of a proper type of stock colour to match it.

A smooth, semi-gloss test slip made in varnish as described, dried in a warm place for two hours, then masked halfway, if *reduced to a really pale tint,* will show decided signs of its comparative fastness after 24 hours in a K.B B. lamp If the sample received is a ready-made paint, it may still be reduced down in a similar manner for this quick first test of fastness. Many reds, maroons, and organic orange and yellow shades, may be matched in a number of ways and the light fastness will often be the surest way of confirming any other tests that, meantime, have been completed.

Much of the actual rubbing out of colour samples for comparison is done by a junior, who should be strictly trained to adhere to the firm's standard methods throughout For instance, if white lead be used for reductions, it must always be used of a standard quality and at a standard ratio for everything—say 20 . 1 of colour (except for making very pale tints for accelerated comparative fading tests). In addition, for these tests (containing mostly white lead, and therefore not varying much in oil absorption), a standard proportion of oil (linseed or castor) should be used for every test. Once it has been decided whether to use linseed oil or castor oil the same oil should always be employed Full strength tests will vary in oil absorption according to the material, but especially with very dark colours, rich in shade, it is essential to use equal ratios of oil to pigment in the "sample" and the "match"

This will give an approximate idea of the comparative oil absorption and ensure a truer comparison of shade Deep, rich colours will tend to appear duller if short in oil, and richer if too much oil be used

If " Reflex " lakes be examined in oil, the proportion of oil used must be the same in both tests, or else big differences in shade are likely to be seen

In evaluating white opaque bases, or yellows (for tinctorial power as distinct from opacity), a blue or a black is often used to show the extent of opacity or " whiteness " in the white, and " yellowness " or tinctorial power in the yellow In such cases, the best all-round colour to use is a weak Celestial blue " struck " at a reduced strength, which can be kept as a standard and always remade to standard when wanted To use carbon blacks or drop blacks, or strong pure blues, for this purpose, often gives misleading results owing to " floating "

Comparative rubbings in oil are of necessity always done at the same time, and put out for examination side by side If a further rubbing be found necessary, after modifying the shade it is better, for the final test, to rub out both the sample and the new test again.

In some laboratories rubbings of colours are put out on slips of transparent celluloid If this be done the celluloid must be carefully chosen, preferably with an inclination to a yellowish tinge, as this kind gives the least alteration of shade Most ordinary sheet celluloid, even if only 5 thousandths inch thick, has a marked effect upon the apparent shade, owing to its peculiar bluish cast Any celluloid used for this purpose should be tried by rubbing on to it samples of pale yellow, pale green and pale blue, then comparing the shades with the same colours on thin picture glass or viewed from the surface instead of through the celluloid A standard way of looking at these tests should be adopted. The author recommends the following as a reliable procedure Use good thin picture glass (14 oz. or less) not too bluish in shade, put out the rubbings in patches of not less than 1 to 2 sq. ins each, and then examine the colours from the back of the glass (standing in a doorway with the back to the light, thus cutting off the top light, is very helpful for accurate matchings of dark colours)

It is essential to keep another sample book, marked " Samples Matched," in which the full particulars should be entered under a number and date. A check sample of the match should then be taken and marked. When such matches are made in the laboratory from colours ground in the works, it is sufficient to blend by grinding in a pestle and mortar, but in the case of colours struck in the laboratory, full allowance must be made for the differences in shade produced by the works grinding plant and that developed by hand grinding in the laboratory. The works product will usually turn out "fuller" and brighter The best way to ensure comparative results is to have a small power-driven granite pan mill, in which laboratory samples may be ground and developed.

Finally, in testing any colours to be matched accurately for any purpose connected with foodstuffs, particular attention should be paid to lead content and freedom from arsenic or otherwise. Regulations are very stringent on these two points. As a rule it is clearly specified if a colour is required to be lead- and arsenic-free, but if this is not known and the counter-sample is quite free from arsenic, it is safer to keep to this in the matching.

Raw Materials

The testing for process work begins with the careful control of the purity and percentage composition of the various raw materials

Some of the "heavy" chemicals that are used in very large quantities are produced in such uniform quality and of such high purity that they are often used absolutely "on trust," that is, without efficient and periodical testing Often it is not realised, however, that serious deterioration of quality may occur during storage in the works, consequently it is essential to check all works materials from time to time. Particular examples of this are referred to below.

Caustic Soda Liquor and Sulphuric Acid For all accurate work these should be tested by actual titration as well as by hydrometer They should be checked off from time to time, if kept in stock for long, and in the case of the former, the percentage of carbonate estimated if the caustic soda is to be used for dissolving dye intermediates.

Soda Ash. Is a remarkably pure commercial article, and contains practically no impurity. It can, however, absorb a moderate amount of *water*, if stored for a long period or kept in a damp situation. If the absorption has been slow, then 5 or 6 per cent of water will make no difference to the *appearance* of the soda ash, but may cause trouble in accurate work The safest plan is to store this in a specially selected dry place

Salt This should be tested for impurities such as calcium and magnesium chloride, which not only render it hygroscopic, but are undesirable in many operations.

Hydrochloric Acid This is one of the chemicals that is often assumed to have a very definite strength, and is not tested often enough All hydrochloric acid used in the works should be carefully tested by hydrometers (with proper allowance for temperature) before being used. Both sulphuric acid and hydrochloric acid, if bought in carboys, are liable to vary from bottle to bottle, and for this reason it is a great advantage to have an acid-proof storage vat in which deliveries can be blended, *and then tested*, before use Acid made by the synthetic process is free from lead and iron and should be used in preference to the " yellow acid," which contains considerable quantities of these impurities

Sodium Bichromate. This is a deliquescent substance and, therefore, needs careful storage and periodic testing. This salt should always be specified " free from uncombined chromic acid."

Acetic Acid. The synthetic type of acetic acid made from acetylene is much to be preferred to that from wood distillation products. The latter type is always apt to contain pyroligneous acid and a small percentage of heavy ketones, and all of these impurities have an adverse effect and leave too persistent a residual odour.

Control of Works Operation

Testing of actual works batches begins with a careful and methodical checking of all materials that have been prepared for the batch. The checking of volume, weights, and temperature (and in the case of solutions, specific gravity) by a practical chemist, should be an efficient safeguard against errors in weighings or calculations A careful inspection of the transmission gear of the stirrer, the valves, etc , of the plant, before starting will often save much delay and trouble In the case of some precipitated mineral colours requiring quick accurate work, this is most essential. Before actually starting, the utensils and test papers, etc , required for the tests or samplings to be done in the works, should all be placed ready to hand and operations begun only when all these are quite ready.

A system of proper washing-down of all vats and refilling, either with a fresh charge or with water if the vat in question is likely to be left for some days, should be adopted. In all cases, where possible, vats should be kept for the same materials. The precipitating vats have generally to be changed from one colour to another, but this change should only be to one of exactly similar type and as near in shade as possible Any exceptionally brilliant clean colour should be made in one vat only, and that vat never used for anything else. A very bright light colour cannot be made satisfactorily otherwise, unless the vat in question happens to be a lead-lined vat, or of glazed earthenware, with a good smooth interior surface

If a chart has been worked out to show the volume per inch and per foot of all vats, then the proper control and checking off of all solutions before finally starting to " strike " a batch of colour is simplified

If during the striking or more particularly during the " finishing " of a " struck " colour, or during the " coupling " of a pigment dye, there is any abnormal behaviour, any alteration in the procedure should be tried out in the laboratory before application to the main batch There are cases where a swift balance must be reached, of faint acidity, or alkalinity, as the case may be In all such processes full provision must be made *in advance* by having the necessary materials to hand to cope with the possible emergency.

When a colour batch has been made and is seen to be quite normal, it will generally need stirring for some time before allowing to settle While this is taking place, all necessary tests can be conducted to see that the batch is exactly to standard.

The manufacture of all colours involving the production of saline mother-liquors which require efficient washing off, should be organised so that the first settling of the colour is as complete as possible (preferably overnight and sometimes longer). Such colours as Chrome yellows, Chrome greens and Iron blues, will settle out more completely in this first liquor than in subsequent wash waters owing to their more dense form at this stage. Some colours, especially Chrome greens and Iron blues, become more and more difficult to settle as the washing water becomes purer.

For colours that are best made by rapidly adding the whole of one component to the other—as is often the case in pigment-dye "coupling"—the stirring must always be very fast and efficient, in order to avoid local excess of the component being added. As a safeguard against an excess of the "added" component being run in, it is usual to conduct the rapid addition (*of these special types*) by running in about 9/10ths or even 19/20ths of the quantity that has been prepared, well mixing, then testing carefully, and adding more slowly the small balance left, after the main batch has been checked and found to be proceeding quite normally. In the case of Chrome yellows, Chrome greens and similar colours, or when precipitating basic dyes on to a green earth suspension, a slow and progressive addition is essential, with a decided retarding of the rate of addition towards the end. When there is no objection to the further dilution of a reagent which is being run into a batch, excessive local concentrations may be avoided by slowing down the rate of addition after half has been added, then when three-quarters of the whole is used, further diluting the remaining quarter and adding this even more slowly

These remarks are purely general and cover a wide range of processes. The actual choice of method must be decided by practical trial on the individual process In later chapters any such special methods or precautions will be referred to in conjunction with actual colour processes given.

A few general remarks on the important operation of "boiling-up" batches are also necessary here. Good agitation is necessary at this stage, in order to obtain a progressive and even development of colour and to avoid localised effect of the steam Boiling-up must always be controlled by actual temperature observation , not by a mere appearance of ebullition, which may very likely be only due to occluded gases or to evolution of carbon dioxide from the solution and, in any case, is very deceptive.

TEST PAPERS

Various kinds of test papers are an essential part of the equipment, before manufacture can be begun and processes controlled Their sensitiveness and their power to distinguish between various types of acidity or alkalinity make a full range of such papers indispensable

General rules apply to all of these .—

(1) Where possible they should be made by the chemist himself at regular intervals, in order to have them fresh

(2) They should be made with very weak impregnating solutions. Strong tints or heavily prepared test papers are not sufficiently sensitive for many operations

(3) Their actual preparation should be carried out in a room quite free from chemical fumes or gases.

(4) They must always be made uniformly, i.e , on one special type of filter paper and with the same strength of impregnating solutions

(5) The best way to keep test papers in the laboratory is in a wide-mouthed stoppered bottle (of brown glass for iodide papers), and for works use a flat tin box as airtight as possible.

The necessary types are as follows —

Litmus Papers The ordinary porous type of papers sold are not at all sensitive, and are almost useless with any colours which stain them and so obscure the tint of the litmus. The type made by British Drug Houses, Ltd , on highly glazed paper is extremely sensitive, and can be used with almost any colour, as after placing a drop of the batch under test on the paper, and rapidly washing off with a wash bottle, the litmus paper will be found to be quite unstained by the dye and to have responded to the most delicate alkaline or acid reaction. They are sold as " neutral " and this type is the most useful, as it serves for tests on either side of the " neutral " point

This reagent of course reacts with even the mildest alkalis and with all acids including carbon dioxide, weak sulphonic acids, etc It is an important guide in making all Lead chromes, Prussian blues, and mixed greens from these two pigments

Brilliant Yellow. In many reactions it is necessary to know when free alkali in the form of caustic alkali is present, as distinct from carbonate alkali " Titan Yellow," made by the Clayton Aniline Co , shows this to a minute degree Papers impregnated with a ¼ per cent solution and dried, have a pale sulphur yellow colour and are practically unaffected by even 10 per cent sodium carbonate They will, however, react giving a brown stain with a solution containing about 1/20 of 1 per cent of caustic soda or potash. In making solutions of beta-naphthol, oxy-naphthoic acid, or other intermediates, or in any process where caustic alkali is to be used and a final end-point obtained at which an absolute minimum of free hydroxyl ions is present, Titan Yellow papers must be used and care taken to see that the correct dye is used for making them so that they react with hydroxyl groups and not to carbonate alkali. Normal sodium beta-naphtholate is strongly alkaline to litmus, therefore Titan Yellow papers must be used to detect free caustic soda in its solution.

Finally, to test for *free caustic alkali* in dark solutions which would mask any test paper reaction, as in making the dye Naphthol green, it is often very useful to add a little pure ammonium chloride to a test portion of the bulk, and heat it, the nose will detect traces of ammonia in this hot test, which indicate extremely small margins of free caustic alkali This is very useful in making Naphthol green direct from the intermediates.

In testing for *free mineral acid* under similar circumstances, a portion of the bulk may be tested by adding a small crystal of pure neutral sodium sulphite, and so arriving at the end-point by repeated tests until only a faint smell of sulphur dioxide is detected; this method is only possible where no substance is present which would react with or oxidise the sulphur dioxide

When it is possible to obtain any of the above-mentioned test papers ready-made, of the glazed quality, they are, generally speaking, the most useful for pigment making work.

Benzopurpurine 4B In all acid reactions where it is desired to distinguish between mineral acid and organic acids, Benzopurpurine 4B should be used. This should be made in very delicate weak shades, as heavily dyed papers are not so sensitive. These should be impregnated in a *hot* 1/10 per cent solution of the dye and must be dried in a clean neutral atmosphere Then they will be very sensitive and react to mineral acids only. They are particularly useful for showing traces of free mineral acid in suspensions or solutions of dye intermediates and in diazotising operations

Starch-Iodide Papers. Starch-iodide papers should be used as fresh as possible They also are best made fairly weak. A good recipe is the following ·

Soluble starch ..	1 gramme.	Shake up in—
Cold water	80 c c	Then add—
Boiling water .	100 c.c	*Allow to cool,*
	then stir in—	
Cadmium iodide	1 gramme	dissolved in—
Water . .	20 c c	

The iodide should not be added to the hot starch solution. Cadmium iodide will keep better in the finished papers than potassium iodide.

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CHAPTER V

INTERMEDIATES FOR DYESTUFFS

TESTS AND PROPERTIES

BEFORE dealing with actual colour-making processes it is necessary to deal with the testing of materials, and the identification of the more important components of samples of colour to be matched Since in special cases the performance of one or two pigment-dye coupling processes has become a recognised part of the work in some of the larger pigment colour factories, methods for a few of the most important of these have been given in this book at full length Among these perhaps the most common are Lithol red R , Helio red R L , Lake red D , Lake red P , Permanent reds 4B and 2B , Lake red C , Ponceau R

Lithol red is made on such a large scale and so uniform in quality by the dye manufacturers that it can hardly pay to make it in the pigment works, but a very successful method is given as a type Lake red D , Lake red P , Ponceau R are seldom made by the pigment makers, are given as representative types, and are indeed regularly made in some pigment works

The first tests given are for the purpose of determining the strength and comparative purity of materials.

BETA-NAPHTHOL

β-naphthol should be bought to a rigid specification, and strict limits fixed for the setting point The most likely impurities are ·

1. Alpha-naphthol.
2. Naphthalene
3. Dihydroxynaphthalene (usually 2 7)
4. Dinaphthyl.

In practice it is seldom necessary to test individually for the presence of any of these impurities The setting point is a sufficiently accurate criterion

The presence of impurities in every case lowers the setting point The usual figure is 119 5° C The melting point is usually about 121° C When necessary the following tests can be made for individual impurities

(1) *Alpha-naphthol* (Callan's modification of Leger's test.) 10 grammes of the beta-naphthol under test are ground up in a glass mortar with 30 c c. distilled water and left for 15 minutes with occasional stirring The test is then filtered and to the filtrate is added, drop by drop, 1 c c of freshly made sodium hypobromite (made by adding 5 c c. bromine to 130 c c. of ice-cold 7 per cent caustic soda solution) Alpha-naphthol if present to the extent of even 0 2 per cent gives a very definite reaction, viz , a red-violet coloration.

(2) *Naphthalene.* 14 grammes of the sample dissolved in 100 c c. of 2 per cent caustic soda at 50° C

Naphthalene gives an opalescent solution and is readily detected by its smell.

(3) *Dihydroxynaphthalene* The presence of this causes the beta-naphthol to darken in colour after storing a few days, or more rapidly on exposure to air 50 grammes of the sample are boiled with 100 c c of water with constant stirring Allow to cool to 20° C and filter The filtrate contains practically all the alpha-naphthol and dihydroxynaphthalene, together with a little beta-naphthol

The solution is neutralised with normal caustic soda (Titan Yellow paper indicator), and concentrated to 30 c c.

Add 15 c c of 10 per cent barium chloride solution The precipitate is washed, dried and weighed, then ignited and the residual barium oxide weighed

The percentage of barium oxide in the precipitate is calculated, and from this an approximate estimate of the percentage of dihydroxynaphthalene in the dried precipitate is obtained.

(4) *Dinaphthyl* The presence of dinaphthyl is due to the condensation of two nuclei during manufacture

It is comparatively insoluble in alkali and on dissolving the beta-naphthol, is left as a fine, slimy, fawn-coloured precipitate.

OXY-NAPHTHOIC ACID

The purity of β-hydroxynaphthoic acid is determined by its setting point, which should not be less than 214° C.

A very pure sample will set between 215° C and 217° C.

The correct melting point of pure 2 · 3-hydroxynaphthoic acid is 216° C Any sample which tests lower than 214° C should be rejected as unsuitable

As this acid is made by heating at a high temperature, tarry impurities are inevitably produced to a small extent in the manufacture, but should have been removed in the refining processes prior to its sale Tarry and other insoluble impurities may all be separated by filtration from a dilute *cold* solution of the acid in soda ash. The total residue should be below ½ per cent

One firm in particular has for some years specialised in the manufacture of this highly important intermediate. and to-day the acid may be obtained without difficulty in a quality of great purity *

R Salt (β-naphthol-3 6-disulphonic acid)

It is somewhat difficult to obtain this free from other sulphonic acids, and it may contain appreciable percentages of the following —β-naphthol 6 8 disulphonic acid (G salt) β-naphthol-3 7-disulphonic acid and β-naphthol 6-monosulphonic acid (Schæffer salt); the probability being in the order named, although commercial qualities are never entirely free from any of them

R. salt used for making any of the simple acid scarlets (Ponceaux), or Pigment scarlet 3B. must be as free from these isomerides as possible, as the presence of any of the isomerides mentioned greatly impairs the purity of the undertone, and reduces the insolubility in water of the lake product. A very simple and reliable test for determining the suitability of the R. salt for making pure, full-tone, non-bleeding reds, is as follows —

Dissolve 0 5 gramme of dry R salt (approximately 70 per cent) or 1 gramme of paste (about 35 per cent average) in 10 c c of water in a 1-in. test tube, and cool.

Add 5 c c. pure nitric acid to which has been added 0 1 gramme sodium nitrite During the first three minutes the colour of the test will gradually become darker If it develops no further than a yellow to pure orange tone the sample is quite suitable for all ordinary colours A sample which gives a decided reddish-orange test in the first minute, or shows a distinct red, is not at all suitable for Pigment scarlet 3B , but may pass for ordinary grades of Ponceau reds

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* British Synthetics Ltd.—a branch of the British Alizarine Co , Ltd , Trafford Park

Any considerable percentage of G salt can be detected by making a *neutral soda salt* of the intermediate, drying and powdering, and then extracting with pure alcohol. Any appreciable content of G salt is shown, as its neutral soda salt is soluble in alcohol, whilst that of the pure R. salt is not.

ANTHRANILIC ACID

Anthranilic acid (for Lake red D. and Pigment scarlet 3B). The best practical tests for this are · (1) The percentage of the acid by titration with sodium nitrite. A good quality should give not less than 98 per cent purity.

(2) Dissolve 6.9 grammes in 200 c c. water with 12 c c of 30° Tw. hydrochloric acid. Stir for 10 minutes, then filter. If there is a large percentage of impurities at this stage the sample may be rejected forthwith. The filtrate is cooled to 5° C. and diazotised by the rapid addition of a 33 per cent solution of 3.5 grammes pure sodium nitrite If the diazo solution (which must give a faint positive test with starch iodide paper) is a pale clear yellow colour and free from tarry matter the quality of the intermediate can be taken as quite good Tarry matter in traces is sometimes present, and can be recognised by the brownish colour of the solution and the unduly dark colour of the dry powder

TOBIAS ACID

Tobias acid (β-naphthylamine 1 sulphonic acid) should be either in the form of granular particles, or if bought as a paste, this should be a " sandy " paste, and not " clayey." The isomerides likely to be present as impurities are Bronner acid (β-naphthylamine 6 sulphonic acid) and Badische acid (β-naphthylamine 8 sulphonic acid) The first named if present will give a distinctly more " clayey " Tobias acid in paste form, and the diazo-Tobias acid will have a deeper yellow colour, inclining to brownish The Badische acid will tend to make the diazo compound of a brighter pale yellow shade, whereas the diazo compound of the 1-sulphonic acid is very pale yellow in colour, inclining towards a very pale buff. The main guide to freedom from these other sulphonic acids is the solubility of the diazo compound in a diazotised test sample *which is only just acid* to Benzopurpurine 4B (" Benzo " test papers). Excess of hydrochloric acid causes undue solubility of all the isomerides of the series The Bronner acid diazo compound is much more soluble than that of the Badische acid, and the pure 1-sulphonic acid diazo compound is practically insoluble The most definite test here, as with many of the intermediates of this type, is to conduct a small laboratory dye coupling to exact and standard figures The shade and appearance of the resultant dye, and the amount of soluble dye or dyes in the filtrate from it, with standard quantities, bulks and temperatures, is a good measure of the purity, for dye-making purposes. In making the diazo compound to the following particulars, the loss of diazo-compound traceable in the filtrate from the diazo-filtration, should not be more than 3 per cent in the case of a good commercial Tobias acid, and in the case of commercially pure acid for Lake Red C should be 1 per cent *as a maximum*

A full description of a laboratory method for carrying out this estimate of loss on diazotisation is given on page 80, under " Special Laboratory Tests."

Another impurity that sometimes occurs in commercial Tobias acid is β β di-naphthyl. This is practically as insoluble in water as Tobias acid, and almost as insoluble in weak acid. Although the di-naphthyl is insoluble in alkali, it is still soluble in the concentrated solutions of Tobias acid in alkali, used when purifying the Tobias acid ready for dye-making—this at a concentration of 14 or 15 per cent will be quite clear, even if the Tobias acid contains up to 2 per cent of di-naphthyl as impurity. Di-naphthyl can be detected, if present to an appreciable extent, by making a 5 per cent solution of the intermediate in caustic soda, then diluting down to 2 per cent with water, when more than about 0 25 per cent of di-naphthyl in the Tobias acid taken will separate from the solution and render it cloudy. If filtered after settling a slimy, fawn-coloured precipitate is obtained. This rather crude but very useful test also indicates beta-naphthylamine if present, but the latter impurity should have been removed by washing the Tobias acid with hot, weak (2 per cent) hydrochloric acid.

As beta-naphthylamine is relatively soluble in hot dilute hydrochloric acid (as compared with its sulphonic acids) it is easy to remove and should never be present as an impurity. It is a most objectionable impurity as it will cause the Lithol red lakes to bleed badly in oil (owing to the presence of some dyestuff without any sulphonic group, produced from the beta-naphthylamine). If its presence be suspected in a sample of Tobias acid, a test should at once be carried out by grinding a 20-gramme sample of the Tobias acid as a paste, with water, using a glass pestle and mortar Then stir in a beaker with 50 c c. 5 per cent hydrochloric acid at 50° C., cool to 15° C , filter, wash, and titrate the filtrate with standard sodium nitrite solution, using starch iodide paper , the total amino-compound found should not exceed 1 per cent of the original amino-compound taken

Of the actual figure obtained, from ¼ to ½ per cent will represent other amino-compounds which will be present as impurities and traces of the Tobias acid which will have dissolved This rough test is a good rapid test for isomerides in " C acid " (page 154) as all the likely isomerides are much more soluble in the warm 5 per cent hydrochloric acid than " C acid " itself The presence of any such isomerides will be readily seen as the diazo compounds show still more marked differences in solubility Therefore as the unwanted isomerides will be found in the filtrate from the diazo compound, their presence will result in loss, but not with any appreciable detriment to the purity of the finished dyestuff if the diazo compound has been made at no greater concentration than that given on page 155, and efficiently filtered

TESTS FOR INTERMEDIATES OF THE ACID AZO SERIES

(1) *Spotting-out Tests.* Spotting-out tests are frequently used for controlling reactions in the works, especially in dye couplings In the laboratory they are used in the titration of naphthols and of phenols with diazo solutions

The test is made by placing a drop of the dye batch on a dry thick filter paper In most cases a colourless rim spreads out from the solid colour If, however, the colour is too soluble at this stage of the reaction in question, a little of the batch is treated with common salt to give a colourless rim.

When the rim has spread about ⅛ in from the solid colour, a spot of each of the two ingredients—diazo-compound, and hydroxy body—is dropped on the filter paper about ¼ in. away. The latter spots gradually spread and a line of dyestuff forms at the junction of the centre spot and the spot of one of the ingredients. The course of the reaction is thus easily followed and in practical hands the tests are extremely delicate

The two essential titrations are

(1) Valuation of primary amino compounds by volumetric diazotisation, using a standard normal sodium nitrite solution

(2) Valuation of naphthols or phenols and their derivatives by volumetric coupling with a freshly made diazo solution of definite standard strength.

The accuracy of the method depends upon the accuracy of the sodium nitrite solution Therefore for both operations the standard sodium nitrite should be made up freshly, about once a month, and its strength determined by means of standard potassium permanganate solution immediately before use. The most readily obtainable pure primary amine is freshly distilled aniline, and a standard solution of aniline in an excess of pure iron-free hydrochloric acid may conveniently be prepared (about once a month). For use, it is mixed when required with an equal volume of the solution of sodium nitrite to form diazo-benzene chloride solution

The two solutions, sodium nitrite and aniline hydrochloride, should be kept in brown glass Winchester quart bottles with rubber stoppers. In this way a minimum of decomposition occurs. They can be safely kept for four to five weeks at least before renewal.

Convenient working strengths are :

(*a*) Sodium Nitrite, Semi-normal (34·5 grammes per litre).

(*b*) Aniline Hydrochloride Semi-normal 93 grammes aniline, 350-400 c.c. pure hydrochloric acid 30° T, made up to 2,000 c.c. with water, this represents 1 equivalent of aniline and 3 to 3½ equivalents of hydrochloric acid Equal volumes (50 c.c.) of each are taken and cooled to 0° C. The sodium nitrite is then added to the aniline hydrochloride, keeping the temperature down to 5° C. This gives 100 c.c. N/4 diazo-benzene chloride, and this should be used within ten minutes of mixing. If kept at 0° C. it can be used up to half an hour after mixing.

In evaluating amino compounds, whether a dry powder or paste intermediate, the strength should first be determined approximately, so that the approximate volume of sodium nitrite required may be known in advance The reason for this is that over 50 per cent of the sodium nitrite should be added rapidly to ensure accurate results with insoluble compounds.

This first rapid addition of sodium nitrite causes vigorous reaction and so facilitates the diazotisation by breaking up the hard particles of Tobias acid or other insoluble amino compound.

Example of test For insoluble intermediates .—Weigh out, for convenience, 1/20 of the gramme-molecular weight of the substance to be tested, e g , in testing Tobias acid (paste, or powder), weigh out 1/20 of 223 grammes (11·15 grammes) of the paste or powder Dissolve this in 100 c c. of warm water (40° C.) with sufficient 10 per cent caustic soda solution to give a faint alkaline reaction to litmus.

If the solution after ten minutes' stirring, and being still alkaline, remains cloudy, it should be filtered and the funnel and filter paper washed into the main test solution. Dilute the solution with ice water to 250 c c. at a temperature of 14 to 15° C. Stir this with a mechanical stirrer and precipitate rapidly with an excess of pure hydrochloric acid diluted with some water (200 c c of acid with 50 c c water is ample)

Continue to stir for about three minutes and then run in from a burette about half the $\frac{N}{2}$ sodium nitrite solution presumed to be necessary Thus if the paste is assumed to be of 60 per cent purity, 30 c c. are to be run in very quickly or, if the intermediate be dry powder, of a purity between 90 and 95 per cent, 45 c c or 50 c.c may be run in quite rapidly.

The titration is then continued slowly, using both Benzopurpurine 4B. paper, to determine the presence of free mineral acid, and fresh starch iodide paper to determine the end point

Very near to this end point the mixture gives a faint lavender test on the starch iodide paper, but the real end point is shown by a very sharp change to a much darker blue-black spot.

The number of c c of $\frac{N}{2}$ sodium nitrite used for the titration gives the percentage of amino compound in the sample tested.

Free mineral acid must be present throughout The test should always be carried out with the use of a mechanical stirrer.

To estimate the loss of diazo compound on filtration of an insoluble diazo precipitate, the filtrate from the test is collected and made up to a definite volume (for example 500 c c.)

A solution of R. salt of known strength is then prepared, taking a quantity considerably more than the diazo compound in the filtrate to be tested, assuming from 5 per cent to 10 per cent present The R salt is made up to 200 c c. with 10 grammes soda ash and water

The whole of the diazo filtrate is poured *into this* with rapid stirring, taking care not to lose any by frothing.

The coloured solution so obtained is saturated with salt and filtered, and the excess R salt in the filtrate is titrated back with diazo-benzene chloride solution The R salt used to combine with the diazo compound in the filtrate can then be calculated.

This general method of testing is quite convenient and accurate for most insoluble derivatives of aniline, toluidine and naphthylamines—especially those containing a sulphonic group. It is not suitable for testing the purity of samples of meta-nitro-para-toluidine

TEST FOR PERCENTAGE PURITY OF META-NITRO-PARA-TOLUIDINE

Take 1/20 of the gramme-molecular weight of the sample if in the dry form, or if it is in paste form, take 1/10 gramme molecule and dry the weighed sample in the oven The dry weight will give approximately the strength, as the dry substance should be of at least 98 to 99 per cent purity

The dried sample is dissolved in 50 c.c of warm (40° C) 80 per cent pure sulphuric acid This solution is slowly poured into 400 c c. of ice water (at 3 to 4° C) and kept stirred by a mechanical stirrer.

The whole of the weighed sample is thus obtained in an extremely fine state of division in the ice water The temperature is kept down to 2° C and 2 grammes of zinc sulphate are added to accelerate the subsequent diazotisation

$\frac{N}{2}$ sodium nitrite equivalent to the estimated weight of the amino compound and 10 per cent in excess, is then rapidly added to the cold suspension of the intermediate.

When the whole mixture has changed to a pale clear yellow solution, free from any yellow specks or flocks, it is further stirred (at a maximum temperature of 2° C) for ten minutes. (The stirring should be fairly slow throughout) The very weak cold solution containing the excess nitrous acid is back-titrated with a standard solution of urea or of aniline hydrochloride, and the true percentage purity of the sample calculated The three essentials are .

(1) Fine suspension of the substance.

(2) Large bulk for test (500 to 600 c c at least for 1/20 gramme molecule test)

(3) Temperature to be kept between 0° and 2° C. throughout.

ESTIMATION OF NAPHTHOLS

To estimate the percentage of naphthol present in a sample of unsubstituted naphthol or of substituted derivatives, such as sulphonic acids, a volumetric dye-coupling test is carried out by the following method —

A sample of the paste intermediate is weighed out—a convenient quantity being 1/20 of the gramme-molecular weight of the substance in question This is dissolved in about 300 c c of water in the case of a soluble sulphonic acid soda salt, or with the addition of 1½ to 2 grammes of caustic soda in the case of a free acid or of a pure naphthol In addition, for any of the three cases, 10 grammes of soda ash are stirred in and the volume made up to a definite figure (for example 400 c.c) with ice, so that the final temperature of the naphthol solution is below 10° C , $\frac{N}{4}$ diazo-benzene chloride solution freshly mixed as described on page 78, and kept in an ice water jacket, is then used to titrate the naphthol. If the dye produced from the substance under test is insoluble, the mixture is regularly spotted on to filter paper and the presence of naphthol in the clear rim from the coloured spot detected by means of a drop of the diazo solution, placed on the filter paper half an inch away from the clear rim, and allowed to " creep " into contact with it As long as free naphthol is still present, a thin line of the colour appears at the line of contact of the two spots The titration is continued until this colour only forms after a second or two, and is quite faint The reaction is then complete and the number of c c of $\frac{N}{4}$ diazo-benzene chloride solution used, divided by two, gives the percentage of naphthol if 1/20 of a gramme molecule has been taken

If the intermediate under test gives a soluble dye with diazo-benzene chloride, when the action is judged to be three-quarters completed, finely powdered salt is slowly added , only enough being used just to ensure a colourless rim

An excessive quantity of salt must not be used

A few examples given below show the method of calculations in these tests —

(1) β-*naphthol.* 7·2 grammes would be taken dissolved in water with 2.0 grammes caustic soda and 10 grammes soda ash.

Assuming that 199 c.c of $\frac{N}{4}$ diazo-benzene chloride are used, the sample contains 99 5 per cent of naphthol mol. wt 144.

(2) *Naphthol monosulphonic acid* (*sodium salt*) (*mol wt* 246) 12 3 grammes would be taken if calculating percentage ultimately as sodium salt, or 11.2 grammes if the calculation is to be made as free acid (mol wt 224).

In either case the number of c c. $\frac{N}{4}$ diazo-benzene chloride used, divided by two, gives the percentage of naphthol present equivalent to a molecular weight of respectively 246 and 224

(3) *Naphthol disulphonic acid as monosodium hydrogen salt* (*mol. wt.* 326). The weight taken would be 16·3 gms , and if 130 c.c. of diazo-benzene chloride were used the percentage, calculated as naphthol disulphonic acid mono-sodium salt, would be 65 per cent

By weighing out 17·4 grammes of the same sample the calculation would show a higher percentage, as more diazo-benzene chloride would be used for the larger quantity and the higher percentage so shown would be the correct valuation as di-sodium salt (mol. wt 348)

Emphasis must be laid on the fact that when buying intermediates such as sulphonic acids of either naphthols or naphthylamines, the basis of purchase and test must be known and specified. For when a substance can exist as either free acid, ammonium,- sodium,- or potassium-salt (or in the case of disulphonic acids, as free acid, mono- or di-salt), there is a great difference in value as will be seen below ·

304 lbs of pure " R." acid (free acid) are equivalent to 326 lbs. of " R " salt (mono-sodium salt), which in turn are equivalent to 348 lbs of " R " salt (di-sodium compound)

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CHAPTER VI

LIGHT AND COLOUR IN RELATION TO PIGMENTS

LIGHT AND COLOUR

SINCE one of the main objects of the pigment manufacturer is to provide his customers with pigments, the colour properties of which fulfil certain more or less definitely specified conditions, a consideration of the effects of light upon colour and coloured objects is a matter of first importance The detailed scientific analysis of the whole of this subject is extremely complicated, and reference should be made to the series of articles given at the end of the chapter, which include an exhaustive bibliography of the subject

Reference should also be made to M Luckiesh ("Colour and its Applications," Van Nostrand, 1927), in which both the practical and scientific aspects of the subjects are dealt with very thoroughly

It is proposed in the present chapter to outline the nature of the problems involved and the efforts to solve them in a practical way.

From the practical point of view the main factors involved may be classified as follows :—

1 The effect of the illuminant upon the apparent colour of the sample

2. The changes in colour produced as a result of chemical or physical changes in the object caused or accelerated by exposure to light

3. The personal factor, including both physiological and psychological phenomena.

It will be readily understood that problems connected with colour change upon exposure are intimately connected with the problems of colour standardisation and colour measurement, for in the absence of a definite and adequate scientific system of measurement we are reduced to describing any colour changes by such vague terms as "faded," "slightly darkened," "rather bluer," and so forth.

The pigment manufacturer is therefore in most cases faced with the problem of matching a sample and so far as possible choosing his pigments to meet the requirements of his customers as regards fastness to light, brightness, strength, and so forth, to say nothing of price The number of problems involved in the question of colour are therefore numerous and may be briefly described as follows —

The apparent colour of a material depends upon .

(*a*) The composition of the light by which it is viewed.

(*b*) The conditions under which it is presented to the illuminant

(*c*) Its environment, i.e , the colour of the surrounding area

(*d*) A personal factor depending upon the ability of the observer to detect differences in colour.

It is evident that any system of colour measurement or standardisation must take all these factors into account, and that all observers must work under the same regulated conditions if the results obtained, whether expressed in scientific terms or by reference to a standard colour, are of general application in the same way as measurements of light, weight, etc.

For the practical purpose of the colour matcher the refinements of the scientific laboratory are not necessary, but the principles must be understood and the conditions of the colour laboratory made to conform as closely as possible to them.

Illumination As colour depends primarily upon the composition of the reflected light it follows that the composition of the incident light is of fundamental importance. Thus an object which appears pure green by ordinary white light would appear almost black in a light which included no green rays

So far as daylight is concerned, its limitations are obvious : it is not consistent in quality nor is it available at the will of the colour matcher. Some form of artificial illuminant therefore is necessary, if consistent results and uninterrupted work are to be achieved

Although daylight varies considerably, we have developed, as a result of experience, a certain power of adjusting our estimation of colour values to correspond with the conditions obtaining at the moment, and we are aware of a certain average quality which we call daylight. It is therefore necessary, as a first step in the solution of colour problems, to agree upon some standard illumination which we accept as representing the average daylight.

It is usually taken that light from a clear north sky is a suitable standard.

For artificial illumination the electric bulb naturally suggests itself The average town supply of electricity is usually sufficiently constant for most purposes, the bulbs are easily obtained and the recognised make reasonably constant

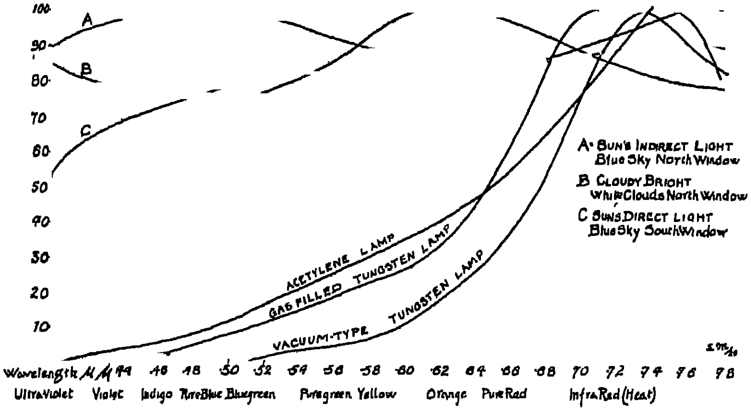

FIG 30 —Curves showing the Discrepancy between Artificial Light and Daylight. (*By courtesy of Messrs Kelvin, Bottomley & Baird*)

Fig 30 shows the intensity curves for various artificial illuminants, and it will be seen that all are deficient in the shorter wave-lengths

The normal filament temperature of the gas-filled electric lamp is about 2,500° C, whereas for the production of white light corresponding to daylight, a temperature of the order of 5,200° C is required. Such a temperature is impracticable, but by running an electric lamp at a higher voltage than it normally consumes, the temperature can be raised to about 3,000° C, at which temperature the light emitted approximates sufficiently closely to daylight to make corrections by filters practicable. In commercial work, glass filters are invariably used, and the intensity curves in Fig 31 give an idea of the degree of approximation obtained in practice. For scientific work, solutions of suitable salts are used (See J Guild, Trans. Opt. Soc., Vol. 27, No. 2, p. 124 1925.)

Conditions under which the Sample is presented to the Illuminant. The composition of the light reflected from a surface is determined by the extent and nature of the absorption of the incident light by the surface.

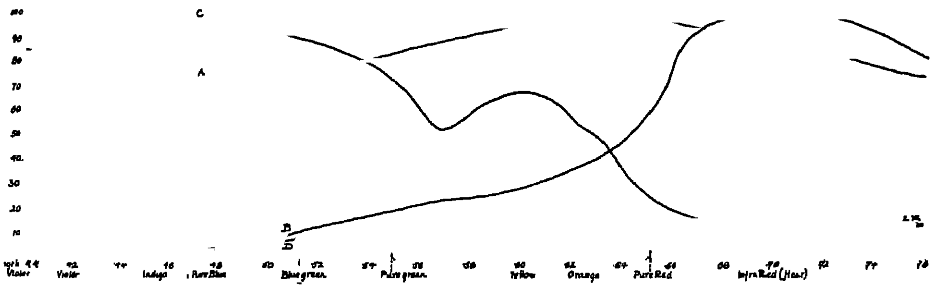

FIG 31 —Transmission Curves of Macbeth Light Filter
A Cloudy White Sky North Light
B Gas Filled Tungsten Lamp
C Percentage of Light passed by Macbeth Filter
D Macbeth Artificial Daylight Compare with Curve A

(By courtesy of Messrs Kelvin, Bottomley & Baird)

Some of the light is reflected almost unaffected, thus producing the effect described as gloss, whilst the rest is only reflected after penetrating more or less deeply into the coloured material A substance may thus present two distinct colour values, known as under tone and over tone ; the under tone depending upon the extent to which the light penetrates the film. This is determined largely by the nature of the medium with which the pigment is ground, the physical condition of the pigment, the extent to which it is diluted with other pigments and the nature of the diluent.

Further, the nature of the surface to which the paint or stain is applied obviously affects the result if the pigment is at all transparent, or the medium absorbed to any appreciable extent

In practice, therefore, it is always necessary to test the colour of a pigment under the same conditions as regards medium, concentration and so forth, as it will be required to withstand in application

The Personal Factor. Apart from these external factors, the estimation of colour is also affected by the physiological and psychological characteristics of the observer Some of these characteristics are common to all observers, whilst others are individual peculiarities The reaction of the human eye and colour stimulus is extremely complicated, and the reader is referred to Luckiesh's book in which the most important phenomena are reviewed Fig. 32 shows the reaction of the normal eye to light of different wave-lengths.

Of what may be termed general characteristics, the most important from the point of view of commercial colour matching are the following :—

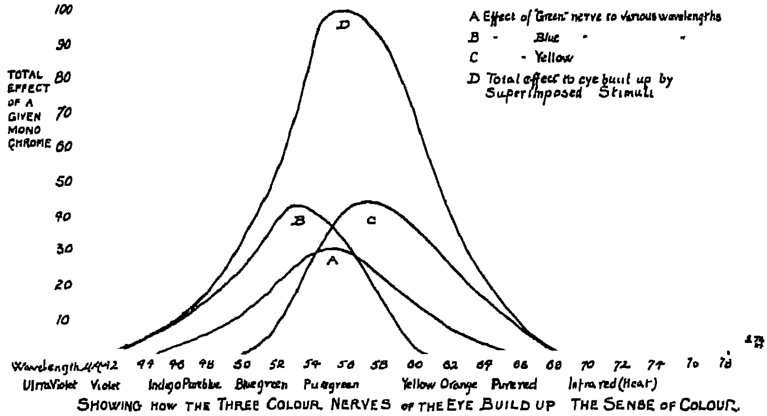

FIG 32 —Colour Sensitiveness Curve of Human Eye

Colour Sensitiveness. The ability to distinguish between light of different colours varies with the wave-length of the light and the intensity of the illumination

The data as to individual sensibility are somewhat contradictory and not sufficiently complete to justify too comprehensive a generalisation. This is probably due to the very complicated nature of the subject and the impossibility of eliminating all the variables, but generally it may be said that the normal eye is most sensitive in the yellow-green spectrum range, and that increased illumination has the effect of making a colour appear less saturated, i e, containing more white The importance of consistent illumination in the matching room and of extra care in dealing with colours at the extreme ends of the spectrum is therefore evident.

Colour Contrast. The eye is generally influenced in its obvious estimate of colour values by the colour of the area surrounding the specimen, and therefore in dealing with patches of colour on a coloured background it is necessary to review the specimen through a mask.

Individual Peculiarities The delicacy of colour perception varies greatly among normal persons, and to some extent with the health and condition of the individual. Persons suffering from jaundice, for example, invariably " see too yellow," whilst excessive tobacco smoking sometimes causes a person to " see too red."

In some cases, however, the divergence from the normal is so great as to amount to a defect rendering even approximate colour matching impossible. Such persons are said to be colour blind Bad cases are of course sufficiently obvious to obviate any danger of the subject being employed in a matching laboratory, but there are frequently more or less intermediate cases in which the " blind area " is so limited that its existence is not suspected until accurate work in a colour laboratory is undertaken

New recruits to the colour laboratory should be therefore carefully observed for a time, before being entrusted with a final decision as to the accuracy of a match.

The possibility of eliminating the personal factor entirely by the use of a photoelectric cell has been investigated, but though the results are interesting scientifically it is not yet a practical proposition The action of the selenium cell depends upon the change of resistance of the element when illuminated The results, however, are rather erratic and the sensibility to different wave-lengths does not agree with that of the eye. Another type depends upon the emission of electrons from the surface of potassium and certain other elements when exposed in vacuo to illumination.

Colour Fatigue Prolonged stimulus of the retina by any one colour, particularly a bright colour, causes fatigue and consequent inability to match accurately or distinguish colours. Normal acuity can be restored fairly rapidly by looking at the complementary colour for a short time. The possibility of errors arising from this cause must be remembered if the matching staff is overworked, or if one man is engaged in a long series of matches of similar bright colours.

COLOUR MATCHING INSTRUMENTS

Having dealt with the various factors which determine our estimate of colour values, the possibility of devising instruments by which colours can be measured under standard conditions and results expressed in terms of universal acceptance may be considered

Numerous instruments for this purpose have been devised. They may be placed in three groups ·

(1) *Subtractive.* In which the light reflected from a standard white surface is modified by passage through standard filters, so that the light finally reaching the eye is of the same colour as that reflected directly from the specimen.

(2) *Additive.* In which standard coloured lights are blended, so that on reflection from a standard white surface the resultant beam is of the same colour as the light reflected directly from the specimen.

(3) *Analytical.* Spectro-photometers in which the light reflected from the specimen is split up into its component rays, the relative intensities of which are measured by comparison with the corresponding rays in the spectrum of a standard white light

The first two obviously depend upon the selection of certain arbitrary units, or standard filters, either for incident or reflected light, whereas the spectro-photometer measures directly in the absolute units of wave-length. This is, of course, more satisfactory from the strictly scientific point of view, but on the other hand the method being purely analytical does not enable the direct reproduction of the colour for visual inspection, which for practical purposes is obviously desirable With experience, however, it is possible to visualise with fair accuracy the colour represented by any particular curve.

(1) *The Lovibond Tintometer.* First made by J. W Lovibond, in 1886, and used by him for a variety of purposes—at first mainly in connection with brewing, but gradually extending to other scientific and technical matters. The instrument was eventually developed to its present form in 1920, and the complete range of glasses consists of 150 standard slips for

each of the three primaries, crimson, yellow and green, these being graded from 0·01 unit to 20 units.

The series of glasses enable one to match any colour as far as hue is concerned, but the instrument is somewhat limited as regards measurement of saturation. The illuminant for which the glasses are standardised is ordinary diffused north light, though an artificial illuminant, such as a "Macbeth" lamp, can also be used. The instrument consists of two tubes through one of which the standard sample is viewed, whilst in the other the coloured glasses are inserted until the colour appears the same in both portions of the field of vision.

The results are expressed in terms of the numbers of glasses used. The units are obviously somewhat arbitrary, but it is quite practicable and for many kinds of work this instrument is used very considerably It is particularly adapted for cases where it is necessary to determine whether or not a particular substance agrees with a standard within certain limits; for example, oils and similar materials are frequently examined in this way, the specification demanding that the colour of the sample shall be between stated Lovibond glasses The same system can also be used in dealing with a particular pigment of which a series of deliveries over a long period has to be made. For general work, however, in a colour laboratory, the range of colours to be matched requires a very large number of glasses, the complete series being nearly 450 slips.

(2) *The Eastman Universal Colorimeter* (Journ. Opt Soc America, 1920 4 420.). This instrument also works on the subtractive principle, the glass slips of the Lovibond Tintometer being replaced by three wedges yellow (minus blue), blue green (minus red) and magenta (minus green) The light from a standard lamp passes through these wedges, and the colour of the transmitted light can be varied by adjusting the wedges so that the light passes through the necessary thickness of each to produce the required colour The position of the wedges is then read off, and together with a record of the amount of white light necessary to produce the required shade, forms a complete record of the colour in question. This instrument was developed during the war and was used largely in connection with work on camouflage.

(3) *The Guild Trichromatic Colorimeter.* This instrument was designed at the National Physical Laboratory, and represents

the most complete attempt so far made to standardise all the conditions which affect the estimation of colour and may be regarded as the most authoritative standard so far produced in this country.

At the present time it is extremely expensive, but in view of the enormous saving in time and trouble that the general adoption of such an instrument would make, it is worthy of serious consideration from all colour manufacturers

Further, an increased demand for the instrument would undoubtedly enable the price to be reduced. The essential features of the instrument are as follows —

The illumination is a standard 1,000-watt tungsten, gas-filled lamp, the current supplied to which is controlled so as to give the filament temperature of about 3,000° K.

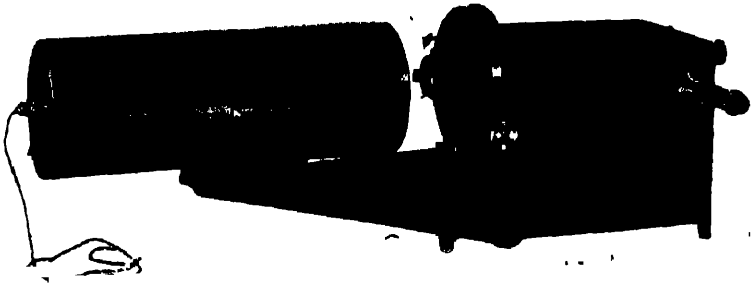

FIG 38—The Guild Trichromatic Colorimeter (General view of instrument without accessories

(*By courtesy of Adam Hilger Ltd*)

By means of a colour filter, consisting of suitable solutions, the light transmitted to the field of vision is equivalent to that from a black body at a temperature of about 5,000° K. The life of the lamp under these conditions is not very long, so that it is necessary to keep a series of standards.

The one in general use can then be checked, say every ten hours, against a secondary standard, which in its turn is checked at intervals against the primary standard

The lamps are standardised by the National Physical Laboratory.

The light from the standard lamp is passed through filters which transmit the colours red, blue, and green Wratten filters No. 71 (red), No. 49B (blue), and No 62 (green), corresponding to wave-lengths 0·63μ, 0·45μ and 0·53μ, are used.

The amount transmitted through each of these filters is controlled by means of slits which can be closed or opened by means of micrometer screws. The readings on the scales attached to the slits are a measure of the intensity of the light transmitted In addition, white light can be passed direct into the field of vision, so that the degree of saturation can also be measured. The four beams of light thus transmitted are recombined by passage through a revolving prism, thus producing a coloured light, which is thrown on to a standard white surface of magnesium oxide, at an angle of 45° and reflected through the eye-piece tube through which is also observed at the same time the specimen to be matched. By adjusting the slits it is possible to produce a coloured light corresponding to that actually reflected by the standard The general arrangement is shown in Figs 33 and 34

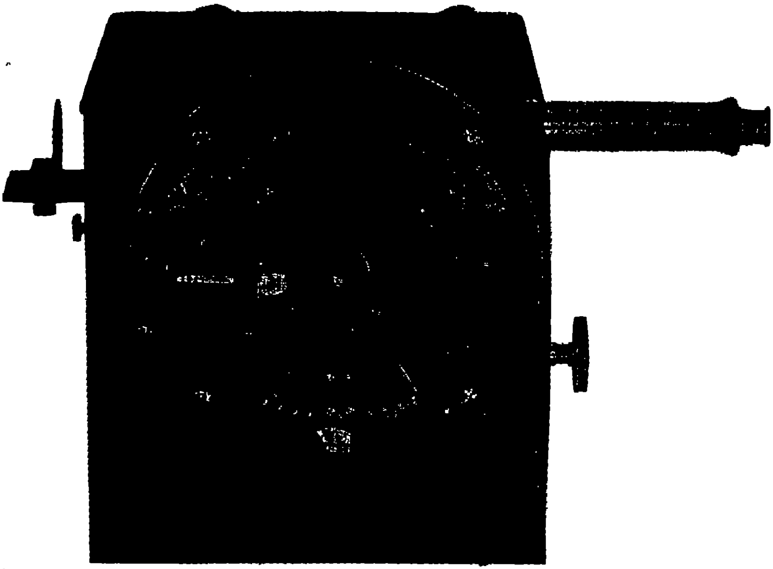

Fig 34 —The Guild Trichromatic Colorimeter Box End, showing sectors
(*By courtesy of Adam Hilger Ltd*)

The instrument is therefore additive in its action, which gives a much greater range of application, whereas the Lovibond instrument is subtractive

(4) *Spectro-Photometers* Instruments of this type are more used in America than in this country They depend upon the

analysis of the reflected light in terms of wave-lengths The light reflected from the specimen is passed through a prism, and the intensity of the light transmitted at various points in the spectrum so produced is determined by comparison with a standard spectrum.

By taking a sufficient number of readings, a graph can be drawn, showing the relationship between intensity and wave-length, the accuracy of which depends upon the number of points determined With the aid of a similar instrument it is possible to reproduce the colour in question by reference to the intensity curve of the standard

Instruments of this type have also been devised by Ives (Phys Rev. 1910, 30, p 446), Nutting (Bul Bur Stds. No 7, p 234, and Bul Bur. Stds 1913, No. 9, p 187) and others

The objection to the spectro-photometer from the industrial point of view is that a large number of readings is required to specify a colour completely, and that the actual colour cannot be reproduced in the instrument A long experience in dealing with such colour curves is necessary therefore before the kind of colour to which the curve applies can be visualised even approximately. Of the various spectro-photometers, the Keufell and Esser instrument is fully described by H. A Gardner Other instruments of this type are the Nutting Spectro-Photometer and the Hess-Ives instrument.

COLOUR CHANGES

The changes with which the colour maker is most concerned are those produced when the colour is exposed to ordinary atmospheric influences and to daylight. These vary widely, and consequently considerable difficulty is frequently experienced in determining exactly what degree of fastness to light a customer really requires. A colour which will prove perfectly satisfactory in a town such as London, may fade comparatively rapidly when exposed for example on the South Coast. In a series of tests made by the writer on printed papers, the colours faded about five times as rapidly in the open country on a test fence at an angle of 45° as they did on a London roof, and about three times as rapidly in the suburbs as they did in the City.

This of course is largely due to the fact that the pall of smoke always present over a large town acts as a light filter removing the ultra-violet rays which are mainly responsible for colour fading.

Apart from the difficulties already referred to, due to the absence of accurate methods of colour measurement, there is also the fact that the action of light upon the colour is greatly affected by the temperature and humidity of the atmosphere; in a perfectly dry atmosphere light appears to have little or no action upon colour

Actual exposure tests are therefore necessary, but at the same time they are of limited significance, moreover, the length of time required to carry them out is a serious defect from the commercial point of view. The development of a standard instrument, in which the various influences causing or accelerating colour changes are reproduced in specified amounts and intensities, is therefore equally as important as the development of scientific and standard colour measurement instruments

FIG 85 —Comparison between Transmission Spectra of Sheet Window Glass and Vita Glass (both 4 mm).
(*By courtesy of Messrs Restlight Ltd*)

As regards the light itself, the rays of short wave-lengths are the most active, and therefore a source emitting a comparatively high proportion of blue and ultra-violet rays is desirable. The mercury vapour lamp and the carbon arc are the most readily adaptable sources of such a light. It is also necessary that any glass interposed between the specimen and the light should be transparent to rays of short wave-length. Quartz can be used, but it is very expensive when comparatively large areas of it are required Recently Messrs Chance and Hunt have developed a special glass known as "Vita glass," which is well adapted for the purpose in question, because it is transparent to the shorter waves of the solar spectrum, as shown in the accompanying figure (Fig 35) The mercury vapour lamp is open to the objection that the light emitted varies very considerably with the age of the lamp and other conditions, and that the rays do not correspond very closely with the solar spectrum, so that the results of the tests, though often similar to those obtained in practice, are sometimes misleading

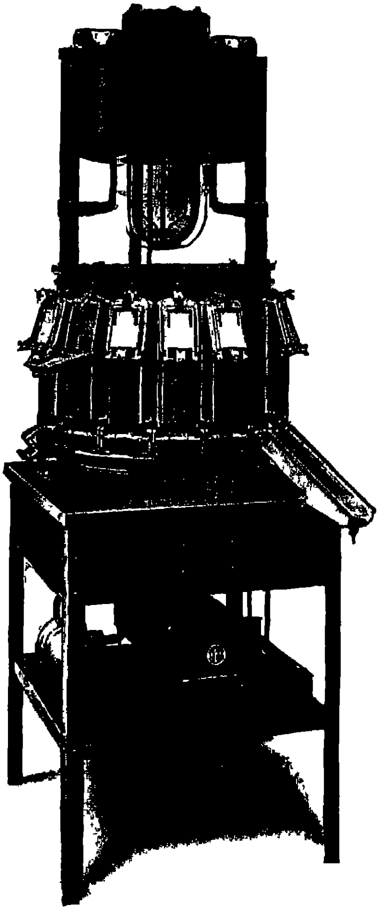

FIG 36 —The Fugitometer
(*By courtesy of Kelvin, Bottomley & Baird*)

The carbon arc lamp used under standard conditions proves very satisfactory as a source of light for colour fading instruments In the "Fade-o-meter" designed by the Atlas

Electric Devices Company, a violet carbon arc is used, the specimens being arranged round it in cases fixed on a metal cylinder. In order to create a moist atmosphere a small fan can be fixed to the top of the cylinder and a basin of water placed at the bottom

As a result of very extensive researches at the Woollen and Worsted Research Association, S G Barker and his colleagues have elaborated this instrument in order to control still further the conditions which effect colour fading It was discovered for example that the degree of humidity plays so important a part in fading, that it may more than counterbalance the effect of the actinic quality of the light Thus some colours were found to fade more rapidly in the moist climate of England than they did in the tropics

In this instrument, known as the "Fugitometer" (Fig. 36), the general construction is similar to that of the Fade-o-meter The specimens are enclosed in small cases provided with Vita glass windows and connected to a humidifier, so that the air circulating through them can be kept at a constant temperature and degree of humidity. In this way all the conditions are standardised and the results obtained agree very closely with those obtained in actual practice, making due allowance for the variation in local conditions

The above resumé gives a general idea of the nature of the problems confronting the pigment manufacturer, and the following list of papers gives fuller details of the various instruments and methods mentioned

The subject is one which is becoming increasingly important, and the practical application of the scientific work, which has been carried out during the past few years, largely depends upon the intelligent co-operation of the manufacturer, therefore a study of these papers in addition to those mentioned in the text is advised.

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CHAPTER VII

TEXTURE AND PARTICLE SIZE IN RELATION TO PIGMENT COLOURS

THE TEXTURE AND PARTICLE SIZE OF PIGMENTS

THE state of division of pigments is a matter of great importance both to the manufacturer and the user.

To the manufacturer, apart from the question of satisfying his customers, it is of importance in that the behaviour of the pigment during its preparation, and consequently the ease or difficulty of handling it, largely depends upon the state of division of the particles Several instances of this are given in the course of this book

So far as the users of pigments are concerned, the question of particle size and texture is of importance in many ways; an even more important consideration in many cases is the relative proportion of different sized particles present, or as it is usually termed, the " size distribution."

The subject has been investigated from many points of view, and during the past few years a great deal of data has been accumulated both from the technical and scientific aspect

Apart from the industries with which this book is primarily concerned, particle size plays an important part in the rubber, photographic, ceramic, cement, and agricultural industries. With such diverse interests concerned with the same subject the data are naturally very scattered, and the writer has particularly referred to an important summary of the literature by J. Parrish (Journ Oil and Colour Chem. Assoc , 1926, 9, 252). In the paint and allied industries, it is obvious that a certain degree of fineness is necessary to produce a smooth and uniform film when the pigment is ground in a suitable medium and applied to a surface As a first classification Noel Heaton suggests the following ("Outlines of Paint Technology," Charles Griffin and Co., 1928) —

(1) *Coarse Particles.* Over 60 microns in diameter.

These are retained by a 300-mesh standard sieve, which is the limit of separation by screens

(2) *Intermediate* Between 10 and 60 microns. These will pass a 300-mesh sieve, but are sufficiently coarse to disturb the uniformity of a paint film and can be detected when the paint (of normal brushing consistency) is carefully brushed out by means of a camel-hair brush

(3) *Fine Particles under* 10 *Microns in Diameter*

The separation and classification of particles on a more accurate and scientific basis than this presents many difficulties, and although great advances have been made in the last few years the application of the results to industrial practice is by no means clear Apart from the question of uniformity in the film, particle size and size distribution have an important bearing on the behaviour of the pigment in relation to the medium In order to form a satisfactory paint, every particle of the pigment must be coated with a film of medium, and the amount required to do this depends largely upon the distribution of particle size For example, if a comparatively coarse pigment and a fine pigment be ground separately in oil to pastes of the same consistency, it is quite possible that on mixing the pastes the resultant mixture will be more fluid than either of the separate pastes, because of the fine particles filling the voids between the large ones and thus reducing the amount of oil required to fill the voids.

As regards the finished product, the size of particles, other things being equal, determines the rate of settling of the pigment. This is a matter of special importance in the production of ready-mixed paints which may have to be stored for a considerable period. The durability of the film and its opacity are also greatly influenced by the size distribution of the particles During the drying of oil paints the medium undergoes considerable volume changes and is subjected to considerable strain. Irregularities due to the presence of coarse particles are, therefore, likely to prove weak points in the film at which unduly rapid breakdown may occur

Cases are referred to in this book in which the fineness of grinding of the dry colour has a considerable influence upon its colour and staining power

In the case of a coloured pigment, the fineness of the particles largely determines the extent to which it can be uniformly distributed over another pigment, usually a white extender or diluent

The development of methods of applying paints other than by brushing has further increased the importance of particle size In spraying paint, the nozzle of the gun is liable to be choked by the accumulation of coarse particles. In the dipping processes, the presence of coarse particles causes specks and blemishes on the surface of the articles out of all proportion to the actual size of the particles The removal of these blemishes greatly increases the cost of the finishing process.

In both spraying and dipping processes, it is also to be noted that there is no mechanical action corresponding to the action of the brush hand in smoothing out the film, and consequently even comparatively soft aggregates will be revealed quite as clearly as hard grits, especially as the films produced by these processes are invariably much thinner than those applied by the brush hand. In the printing trade, fineness of particles is a matter of first importance, since the success of a printing ink depends upon its ability to print clearly and sharply the finest details from the plates In half-tone processes the block is covered with minute dots, as many as 250 and even 300 to the inch, and the clearness of the print depends upon each dot giving a sharp and clear impression The presence of even a small proportion of coarse particles is obviously disastrous from this point of view. In the planographic processes, such as lithography and the " offset " process, the design is printed from plane surfaces, and consequently the ink must give a perfectly uniform and smooth film, which is extremely thin

Apart from these considerations, the presence of any hard particles greatly increases the amount of wear on the plates, and as these are often expensive this is an important matter. The question of time is often more important than that of money, for the printer invariably has to work to a time-table and delays are, therefore, very serious In the rubber industry, it has been found that size distribution of the particles of the pigments used has a determining influence upon the elasticity and tensile strength of the product In this case the medium with which the pigments are incorporated is extremely viscous and consequently any true grinding action is practically out of the question. The manufacturer has, therefore, to supply the pigment in a suitable form, and cannot rely upon the rubber manufacturer to effect any improvement in respect to particle size. Even in paint and allied industries the term " grinding " is somewhat of a misnomer, because the action of the mill is largely confined to the breaking up of large aggregates and thoroughly coating all the particles with the medium. Comparatively little reduction in actual particle size occurs during the process.

From the above it is evident that some knowledge of this subject is of first importance to the pigment manufacturer, for although the pigments dealt with in this book are made by precipitation processes and, therefore, the ultimate particle size invariably falls well within the limits suitable for the industries in question, it will be seen from the instances given in the book that formation of hard aggregates, which in practice act as particles, is very liable to occur as a result of unsuitable methods of precipitation and subsequent treatment of the precipitates Apart from this, there is the possibility of grit and extraneous matter being introduced to the pigment, and in cases where a mineral, such as barytes or silica, is incorporated in the lake, the question of particle size must be considered in selecting a suitable grade.

In the study of particle size, the first step is obviously the separation of the pigment into groups of particles in which the size distribution falls within more or less definite limits.

Screening. The most obvious method is the use of screens The value of this, however, is limited on account of the fact that the practical limit in sieve manufacture is about 300 mesh, which will pass any particles of less than 60 microns diameter, and, for the purposes with which we are concerned, particles only become of interest when they are well below that limit. The British Engineering Standards Association specifications invariably include a clause demanding that only a comparatively minute proportion (0.5 to 1.0 per cent) shall be retained by 200 I M.M standard sieve. This corresponds to a diameter of over 70 microns and, therefore, merely guards against the presence of large grits and aggregates due either to defective methods of manufacture or to the introduction of extraneous impurities

There is also the objection that it is practically impossible to guarantee that no hole in the sieve shall be distorted or a mesh broken A single enlarged hole can let through an unlimited number of particles especially when the pigment is washed through by a liquid, as recommended in the British Engineering Standards Association specifications for pigments.

The limitations of screening are at least considerably reduced in the apparatus designed by G Gallie and B. D. Porrit, in which the pigment is washed through a sieve by means of a jet of water at high pressure. The sieve forms the bottom of a conical vessel and is about one inch in diameter, whereas in the ordinary way of screening a diameter of about three inches is required. Calibration of the sieve is thus facilitated and the chance of error, due to the distortion or breaking of a mesh, is much reduced (Journ. Oil and Colour Chemists' Association 1926, 9, 235)

Sedimentation This method depends upon the settling of particles from a suspension in a suitable liquid. Other things being equal, the rate of fall of the individual particles in the liquid approximately follows Stokes' law. By shaking up the pigment in the liquid and then observing the rate at which the sediment forms, an idea of the relative sizes of the particles can be obtained, and, by removing portions of the suspension at different stages of the settling, the particles can be separated into groups of various average sizes and these can be further examined microscopically. Such a separation is of course incomplete, as obviously the fine particles, which happen to be near the bottom of the vessel at the beginning of the test, will come to rest on the bottom before the larger particles, which, although falling at a greater rate, are nearer the top and consequently have further to travel

By the adoption of various modifications in the apparatus and the application of rather complicated mathematical processes to the experimental data, very useful deductions can be drawn. The method has been very largely applied to the examination of soils with valuable results, and the reader is referred to various papers given at the end of this chapter

Elutriation. This method has been largely used in connection with pigments and, when carried out with due care, undoubtedly yields very valuable information.

The process was first introduced by Schone, whose apparatus consisted essentially of a long conical vessel through which a constant stream of the elutriating liquid was passed, carrying with it such particles of the substances under test as were so small that their rate of fall was less than the upward rate o flow of the liquid

A simple apparatus of this type was designed by T. M Lowry (Journ. Oil and Colour Chemists' Association 1922, 5 22) for use in connection with the grinding of barytes. For the examination of pigments generally, a rather more elaborate apparatus is needed and considerable care is necessary, both in the choice of the elutriating liquid and the proper dispersion of the pigment in it.

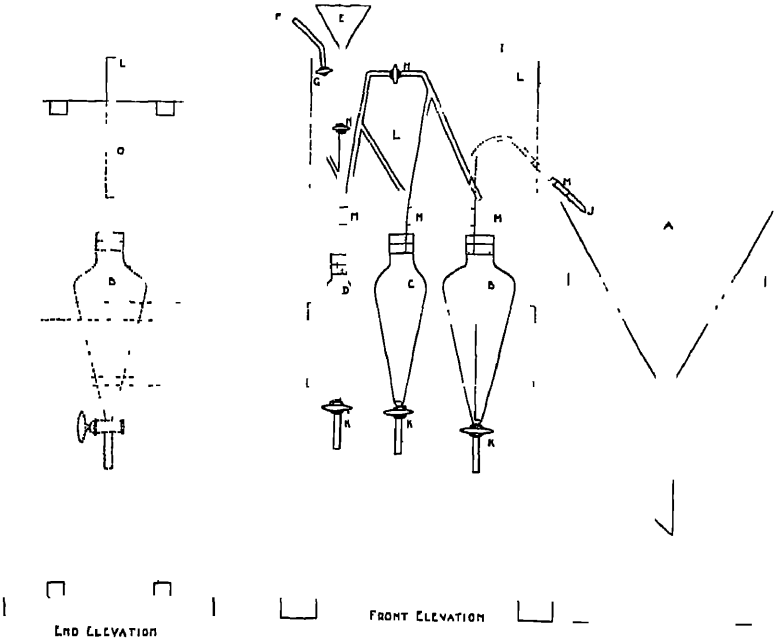

FIG 37 —The Brimsdown Elutriator (See key on next page)
(*By courtesy of C A Klein*)

The apparatus shown in Fig. 37 is that at present used by C. A Klein and embodies several improvements on the older model

The provision of taps at the bottom of each elutriator enables the various fractions to be removed easily The introduction of the pigment at the top of the first elutriator whilst the apparatus is actually working, ensures a more thorough and rapid dispersion of the particles. The apparatus is also more compact and is easier to manipulate than the original type

KEY TO FIG 37

A	12in diameter funnel to take 50 cm fluted filter paper (Whatman No 3)
B	Elutriator tube Internal diameter 4 ins
C	Elutriator tube Internal diameter 3 ins
D	Elutriator tube Internal diameter 1½ ins
E N	Tap funnel for introducing powder into the apparatus
F G	Inlet and regulating tap for the elutriating medium (from constant head apparatus)
H	Three-way tap for removing air bubbles from the apparatus
I	Pressure gauge
J	Standard jet
K	Taps for emptying elutriator tubes
L	Board for supporting glass connections, the latter being sunk into the wood for protection The exit tube is sunk into the back of the board for convenience The board is removable for cleaning purposes
M	Rubber connections
O	Slot cut in the side of the framework to allow for the passage of the exit tube

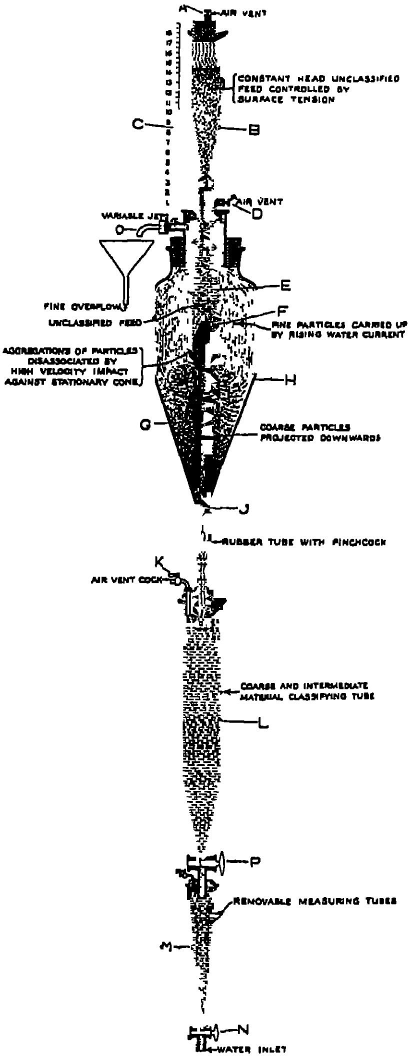
A
AIR VENT
CONSTANT HEAD UNCLASSIFIED FEED CONTROLLED BY SURFACE TENSION
C
B
AIR VENT
D
VARIABLE JET
O
E
FINE OVERFLOW
UNCLASSIFIED FEED
F
FINE PARTICLES CARRIED UP BY RISING WATER CURRENT
AGGREGATIONS OF PARTICLES DISASSOCIATED BY HIGH VELOCITY IMPACT AGAINST STATIONARY CONE
H
G
COARSE PARTICLES PROJECTED DOWNWARDS
J
RUBBER TUBE WITH PINCHCOCK
K
AIR VENT COCK
COARSE AND INTERMEDIATE MATERIAL CLASSIFYING TUBE
L
P
REMOVABLE MEASURING TUBES
M
N
WATER INLET

FIG 38 —The Kinetic Elutriator
(*By courtesy of Kinetic Elutriators Ltd*)

In this apparatus, the series of elutriators of varying diameter is arranged to separate particles into a series of groups of definite size distribution. The rate of flow of the liquid through the apparatus is controlled by the use of a series of standardised jets, which can be attached to the last vessel of the series As a further check on processes, a pressure gauge is attached to each elutriator It is thus possible to deal with the wide variety of particles and to separate them into definite groups Generally speaking, methylated spirit has proved to be the most suitable elutriating liquid, except in cases, unfortunately comparatively few, where water can be used The pigment is boiled for about two hours with the liquid to ensure both a thorough wetting of the particles and their dispersion in the medium In the hands of Klein and his colleagues, this method has proved extremely valuable, especially when used in conjunction with a careful microscopic examination of the various fractions.

Andrews Kinetic Elutriator In the elutriator designed by L. Andrews (Fig. 38), the powder is introduced at the top and thus meets the current of the elutriating liquid passing upwards. The apparatus is so designed that the particles are subjected to the maximum amount of agitation and separation is comparatively rapid In some cases an hour and a half is sufficient to produce the same degree of separation as twenty-four hours in the usual type of elutriator. This apparatus is used in several industrial processes as a means of works control, and it is particularly useful in cases where a rapid separation of comparatively few grades is required—as, for example, in determining the proportion of over-sized particles obtained in grinding such substances as barytes, silica, etc , on a commercial scale

Microscopic Examination Whether preceded by elutriation or not, the microscopic examination of pigments is a matter of importance.

In order that the microscope shall give a true picture of the state of division of the pigment, it is obviously essential that the pigment shall be properly dispersed, as otherwise aggregates may well be mistaken for particles

As in the case of elutriation, the selection of a suitable medium is important, for with an unsuitable medium aggregation may occur, giving a totally false impression of the real state of the pigment. In the case of white pigments, the refractive index of the medium should be as widely different from that of the particles as possible, in order to obtain the maximum visibility of the particles. Noèl Heaton suggests thoroughly dispersing the pigment in a gelatin solution, which is then suddenly cooled, so that the particles are not allowed time to flocculate before the medium sets Very satisfactory slides can be made by this process and these have the further advantage that they can be kept indefinitely. Canada balsam also can be used. For samples of temporary interest, H. Green's method is very useful

The pigment is rubbed out on a microscope slide with turpentine, continuing the rubbing action until the turpentine has evaporated. The pigment is thus left finely distributed over the slide. With white pigments, the use of a gramophone record is a very rapid and successful method of preparing a specimen The pigments are rubbed across the ridges in a broken record, and each ridge retains some of the particles which can readily be examined with the microscope against the black background.

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SECTION 3

INORGANIC PIGMENTS

CHAPTER VIII

Chromate Pigments

LEAD chromates of various types and shades form a group of heavy dense pigment yellows ranging from pale primrose to deep orange-red, according to the method of production Owing to the many valuable properties of these pigments, such as opacity, low oil absorption, ease of grinding, relative inertness in most media, and high resistance to weathering and to the action of light, they are used to a greater extent than any other type of pigment. In combination with blues to form Chrome or Brunswick greens they are used to an even greater extent than alone The Chrome yellows and greens form excellent weather-resisting pigments for outdoor paints, and are only restricted in their use by two considerations · (*a*) They are not alkali-resisting and therefore cannot be used on walls or cement, where free lime or other alkali is likely to be present. (*b*) They are browned or blackened in certain districts in towns and manufacturing centres where sulphuretted hydrogen is always present in the atmosphere

It is quite possible that in time pigment dyes will be produced, which are able to supersede the lead chromes and overcome the two defects of this class (lack of permanence to alkali and to the action of sulphuretted hydrogen). At present this is not possible at an economic price, and the use of a range of such pigment dye shades is mostly restricted to cases where the presence of lead is objectionable or prohibited

The normal lead chromate ($PbCrO_4$) is of a bright medium yellow shade and generally forms at least 90 per cent of the constituents of a good pure middle Chrome yellow. The paler shades are obtained by precipitating the normal chromate on to varying proportions of lead sulphate, which is usually precipitated at the same time in the mixture The orange to red shades are obtained from the normal chromate with varying proportions of basic lead chromate ($PbCrO_4.PbO$), the redder shades consisting entirely basic lead chromate.

The chief considerations in making primrose and lemon shades are to see that the ingredients and method ensure sufficient lead sulphate, and that the sulphate and the lead chromate formed are both in a fine state of division These points will render the production of a suitable shade fairly simple. To retain this shade as a permanent colour in the finished product is not, however, so easy nor certain, but generally speaking it may be said that the main safeguards are a definite excess of mineral acid throughout the striking process and washing, so that a faint excess of free mineral acid is still present in the wet press cakes Organic acids should *not* be used to acidify lemon and middle Chrome yellows after striking, as "blackening" of the shade will very probably occur. The opposite is the case when the same pale chrome yellows are struck as combined shades with "iron" blues to give Chrome greens. In these cases tartaric acid is generally an essential addition after striking the colour, in order to retain the brightness. The curious greying effect that some organic acids give to pale shades of Chrome yellows, on drying in the ovens, is probably responsible for the fact that pale chromes made from lead nitrate are generally more stable in the oven than the same shades from lead acetate

Normal lead chromate can only be produced in acid solution, and therefore cannot be made from normal potassium chromate (K_2CrO_4), unless of course, mineral acid also be present to counteract the basicity, otherwise red shades will be obtained As the basic salts are produced by the interaction of litharge with normal lead nitrate or acetate as the case may be, forming $Pb(NO_3)_2 . PbO$ and $Pb(CH_3COO)_2 . PbO$ respectively, they are a cheaper source of lead than the normal salts and so are used wherever possible, for the formation of yellow chromes. Using bichromates with these, the acidity of the bichromate counteracts the basicity of the lead salt. In the cases where the still less soluble basic lead compounds are used, i e , the basic chloride and carbonate, even with bichromate of soda or potash, additional mineral acid has to be employed

The medium and pale shades are usually made with solutions of about 20 per cent strength and the bichromate is always added to the lead solution. This addition has to be made very slowly if good results are to be obtained, and a slight excess of lead must be left in solution.

Orange and Red Chromes These shades varying from light orange to orange-red are all produced by reactions in which the basic components predominate. The more basic the components, the redder the shade of the product, basic lead carbonate giving about the reddest shade of all. These pigments are usually made from stronger solutions than are the middle shades and they are struck at the boil Unlike the middle and pale shades, which should be finished with a slight excess of lead in solution, the redder shades are finished with all the lead precipitated and usually with a slight excess of sodium chromate in solution In the case of the orange and red chromes the order of addition may be reversed, i e , the lead salt may be added to the bichromate.

Washing and Finishing of Yellow Chrome Pigments The time occupied in washing to the specified freedom from saline matter and excess acid, and the exact degree of excess acidity or of soluble lead compound, all play a great part in retaining the proper bright shade of the pigment during and subsequent to drying

The best procedure for pale Chrome yellows is to fill up the vat with water half an hour after striking, slowly stirring all the time, and then allow to settle overnight The top liquor is run off as far as possible the next day. The second and third filling and running off should be done slowly, allowing plenty of time to settle, so that a lapse of two full days occurs before filtering. Even if the chrome be washed free from saline matter, and contain only the minute trace of free acid advisable, it is best to wait the full two days before filtering and drying.

In this way the final stable shade is slowly attained prior to drying Unless stability of shade is secured at this stage the change will continue in the filter-press and in the drying oven, and cause more dulling of the shade than would occur naturally during the standing and washing

As regards the end point of the colour striking, a distinct excess of lead and of mineral acid at the end of the reaction is essential for primrose, lemon and middle shades of chrome, in order to avoid darkening and reddening of the shade of the finished product during washing and drying. Excess bichromate is therefore fatal. On the other hand, excess mineral acid during drying gives a soapy or " silky " appearance to the chrome when it is ground in oil In the case of orange chromes, depth of shade depends on two main factors .

1. The basicity of the ingredients.
2. The duration of the boiling.

The actual shade desired is usually judged by careful observation and the boiling process is stopped at the point judged to be correct There is very little darkening in shade of these chromes during the drying. Those made in distinctly alkaline mother liquors must be very well washed, otherwise they dry off too hard in the oven and are unsatisfactory for use in paints.

Filtering and Drying. The best all-round method of filtering lead Chrome yellows is on a vacuum filter. They should be filtered as free as possible from water, so that drying will be rapid. Rapidity of drying is an important factor in keeping the pale shades bright—that is provided it is attained by preparing *well-pressed* cakes, which are properly broken up and placed on wooden trays in a well ventilated hot air oven. If the quick drying be secured merely by "stoving" at a higher temperature, the shade will generally be duller and darker. A well-made chrome of middle or lemon shade can be dried at 105° C quite successfully, but for very pale, bright lemon and primrose shades 90° C. to 95° C is much safer. When these two latter contain alumina precipitated in the process, rapid drying at not above 85° C to 90° C. is necessary and is best effected in a vacuum oven If a hot air oven is used, the press cakes must be well broken up and the temperature never allowed to exceed 90° C. to 95° C

Size of Batches Owing to the high specific gravity of the pigment, lead chromes can be made in batches of half a ton for the palest shades, which contain a large percentage of lead sulphate. The process can be carried out satisfactorily in vats ranging from 2,000 to 4,000 gallons capacity, except when alum or aluminium sulphate is used in order to give a fine bulky product In the latter cases rather less material can be handled in one vat.

Orange chromes up to 4 or 5 cwts. may be produced in vats of 800 gallons capacity, because the product is dense and is made in concentrated solutions. They are usually made in moderate sized batches for steam economy in the boiling up.

In the following pages a few actual formulæ are included, with the quantities of the ingredients, but most manufacturers will have their own modifications to suit their particular needs.

The processes referred to here all involve the use of basic lead salts : basic acetate, basic nitrate, or basic chloride. In modern practice the more costly normal salts are seldom used in making yellows, although they are often employed for bright " mixed " greens (lead chrome and Prussian blue).

General considerations governing the production of Chrome yellows and greens are as follows :—

1 Strong heavy stirrers are required and efficient, reliable transmission of power.

2. All stirring must be as fast as possible and always carried out at a standard rate , 35 to 40 r p.m. in a 7-foot diameter vat may be taken as a good standard rate for these heavy colours This speed should be checked occasionally on all vats to see that there is no falling off in power and speed.

3 Footstep bearings are essential for the stirrers in vats used for these heavy pigments

4 Standard strengths of solutions and temperatures should always be adhered to—" Normal " temperature may mean 5° C in winter and 20° C. in summer It is preferable to fix it definitely all the year round at 16° C. for the actual solutions at the time they are used.

5. Every stage of settling and washing off of the pigment should be carried out to a definite point as regards the *depth to which the pigment settles at each stage* before running off Haphazard running off of top liquors usually leads to erratic results in the final product. The saline content will vary greatly with each washing if the first run-off, in particular, is not done to a standard "depth," and this may affect the subsequent physical condition of the pigment.

6 If any batch of lead Chrome yellow (except orange) or green should show a deficiency of soluble lead at the end of the precipitation, sufficient acetate or nitrate must at once be added to give the necessary excess of lead.

7 In making chromes from basic lead salts, injudicious addition of water during the early stages of the precipitation of lemon and middle chrome shades may produce some lead hydroxide, the presence of which always causes greying or " blackening " of the shade during drying. Incautious addition

of soda to neutralise acid, in order to shorten the time of washing, has the same effect.

8. The general rules which govern the choice of the type of "sulphate" to be used as a precipitant for producing the lead sulphate in lemon and primrose chromes, and in Chrome greens, may be summarised as follows :—

(*a*) *Glauber's Salt* gives dense slimy precipitates of high specific gravity and low oil absorption. Some Glauber's salt, therefore, is included when it is necessary to secure these properties.

(*b*) *Alum* gives a soft and flocculent precipitate with a slightly greener tone to the chrome. Used alone it gives a product not quite so easy to filter. Alum is, therefore, more often used with Glauber's salt or sulphuric acid than alone.

(*c*) *Sulphuric Acid* gives a still greener final product, which is rather slimy and hard to filter. It is best used in conjunction with some alum.

Primrose Chrome Generally speaking this shade of chrome is obtained by the inclusion in the formula of sufficient lead salts and sulphates to produce at least 45 per cent of lead sulphate in the finished product. Paler shades contain even more, but there is a limit to obtaining bright, pale shades simply by increasing the percentage of lead sulphate formed In these paler shades the brightness is retained by using some aluminium sulphate, and so obtaining a finer and softer precipitate. This aluminium appears in the final product as aluminium hydroxide, which is allowed in the B E.S.A Specification No. 282 (1927) for primrose chromes

"*Acetate*" *Primrose Chrome Formula* Run 190 lbs 80 per cent acetic acid into 400 gallons of water in a 2,000 gallon vat and add slowly, with intensive agitation, 600 lbs. of finely powdered litharge Continue to agitate vigorously for one hour, then test to verify that all traces of lead monoxide have been converted into basic acetate or acetate (the resultant suspension being a mixture of the basic acetate and normal acetate).

Proceed to run in the following mixture very gradually, slowing up considerably towards the end —

Sodium bichromate ($Na_2Cr_2O_7\ 2H_2O$)	145 lbs
Aluminium sulphate (18% Al_2O_3)	105 ,,
Sulphuric acid 95%	50 ,,

dissolved in 150 gallons of water

As soon as this mixed bichromate solution is all added, begin the addition of 100 gallons of 10 per cent sodium carbonate solution. The whole of this may not be required. The addition is continued slowly until the acidity to benzopurpurine 4B. paper (see p. 70) has disappeared. The final temperature (if started at 16° C.) will be about 18° C. The remaining acid is removed by the washing process. There must be distinct excess of lead in the first wash water. The batch is stirred *slowly* for half an hour before the vat is filled right up. The pigment is then allowed to settle for at least 18 hours before the first run-off. It is then washed according to a standard plan until only a mere trace of acid remains in the clear liquor (glazed litmus test, see p 69)

"Nitrate" Primrose Chrome. The following process will yield a pale, bright shade, rather more stable in drying and rather better in density than those produced by the acetate process Using the same plant as in the acetate process just described, a somewhat smaller batch would be made. A typical formula is as follows —

Lead nitrate	200 lbs.
dissolved in—	
Water	200 gallons
then add—	
White lead (finely powdered)	175 lbs.

The white lead is kept in suspension by very vigorous stirring This operation should be performed in a separate vat and the mixture passed through a hair sieve into the coupling vat, to ensure that no large grains of white lead remain. After 15 to 30 minutes' stirring, slowly run in :

MIXED BICHROMATE SOLUTION

Sodium bichromate ($Na_2Cr_2O_7$ $2H_2O$)	75 lbs.
Aluminium sulphate (18% Al_2O_3)	92 ,,
Water	80 gallons

When this has been run in and the whole well stirred, a further gradual addition of 23 lbs. aluminium sulphate in 12 gallons of water is made Finally the batch is finished by the addition of a 10 per cent solution of sodium carbonate as described in the case of the acetate process (p 116), and not more than 30 gallons should be required.

The white lead in this method gives a much softer product than that obtained by the acetate process and keeps the excess acidity down during the process, thus preventing "silkiness" of the final chrome when ground in oil

"*Acetate*" *Lemon Chrome*. The general method is the same as for the *corresponding primrose shade*, but the excess of acid may be less. The concentrations of solutions are rather lower for a good lemon chrome, i.e, approximately 15 per cent, and all are used at 16° C.

Materials required

Powdered litharge	400 lbs
Acetic acid	125 ,,
Sodium bichromate ($Na_2Cr_2O_7$ $2H_2O$)	200 ,,
Aluminium sulphate (18% Al_2O_3)	60 ,,
Sulphuric acid 95%	5 ,,

This gives a good greenish-lemon shade.

"*Nitrate*" *Lemon Chrome*. In this case white lead is used as for the primrose shade, but in place of lead nitrate, nitric acid is used The nitric acid and white lead are boiled up together with half of the water and then cooled by adding the remainder, the quantities being as follows :—

White lead 400 lbs. suspended in 80 gallons of water and passed through a fine sieve, then 350 lbs. nitric acid D (1.350) are run in and the mixture boiled. The mixture is then made up to 160 gallons and cooled to 18° C The following mixed bichromate solution is run in as for the previous processes .—

Sodium bichromate ($Na_2Cr_2O_7$ $2H_2O$)	120 lbs.
Glauber's salt crystals	80 ,,
Water	200 gallons

As will be seen, this is a very concentrated batch and needs good stirring. It must be made as cold as possible, not above 18° C. in any case When all is well stirred in—

Soda ash	83 lbs

in a fine, dry form is very gradually sifted into the well-stirred batch Stirring is continued for half an hour, then the batch is filled up and finished as before indicated

This method gives a fine dense colour of bright shade and fairly low oil absorption, which is very suitable for use in cellulose enamels. In fact it may be generally stated that the nitrate Chrome yellows are the best for use in cellulose work.

"Acetate" Middle Chrome. As this is approximately a pure normal lead chromate, the manufacture is quite straightforward and the only precautions necessary are

1 Excess lead must be present at the end of the striking operation

2. Some small percentage of mineral acid, usually sulphuric acid, must be used in the formula.

3. The pigment must be washed quite free from acid before pressing and drying. In making this pigment, as in all the other shades, the addition of the bichromate must be fairly slow and especially so towards the end of the operation.

The following are suitable quantities for a batch, all solutions being approximately 20 per cent strength .—

Powdered litharge	400 lbs
Acetic acid (80%)	125 ,,
Sodium bichromate ($Na_2Cr_2O_7$ $2H_2O$)	237 ,,
Sulphuric acid 95%	2 ,,

"Nitrate" Middle Chrome Middle chrome made by the nitrate method is very bright and strong, but costs rather more to make. If the process is carefully carried out, and the white lead properly converted into basic nitrate, the texture is soft and oil absorption relatively low. In this case again very intensive stirring is necessary and some method of properly subdividing the white lead must be used, such as straining a suspension of the white lead in water through a fine hair sieve before adding the lead nitrate. The following quantities will produce a good medium shade —

Lead "Solution." 600 lbs. dry white lead, well subdivided and suspended in 300 gallons of water, sieved into—

600 lbs lead nitrate in 400 gallons of water.

Bichromate Solution 522 lbs. sodium bichromate in 500 gallons of water.

1 lb Sulphuric acid 95%

The colour is finally washed free from acid before drying

"Basic Chloride" Chromes. These form a class of cheaply made chromes which can be produced in lemon, middle and orange shades of good colour and texture. They require special plant and methods, and are much more difficult to control than

the basic nitrate or basic acetate types. The reason for their cheapness is that the cheapest possible sources of lead and of chlorine are employed, i e , litharge and common salt. The two initial difficulties are :

1. That the basic chloride is not produced as a fully completed reaction, except in high concentrations and in warm solutions.
2. That the litharge and the basic chloride are both heavy and insoluble bodies. This fact, taken in conjunction with the relatively slow progress of the reaction between the salt and the litharge, necessitates the use of a high rate of efficiency of stirring during the production of the basic chloride. This rapid stirring in such a heavy mass requires careful design of plant and entails a high consumption of power

The best type of vat for this is a sound oaken vat of fairly small diameter, with a stirrer of very strong cross-section and construction. An arrangement of several thick stirrer blades set spirally, and not too wide in the blade, gives the best results. A vat 4 ft. 6 ins. in diameter and 5 ft. high will be about right for a half-ton charge. .

The rate of stirring in this particular size should be at least 50 r.p.m. A substantial footstep made of acid and alkali-resisting metal is essential.

Owing to the heavy wear on such a plant, the production of basic lead chloride for chromes has been carried out by some manufacturers in cast-iron pan mills and mixers. These two methods give a finely divided product and a complete reaction, but heavy corrosion of the cast-iron plant is inevitable, owing to the action of the nascent caustic soda formed during the reaction.

The success of this basic chloride process is more a question of ingenuity in plant design and painstaking care in its maintenance, than of the actual formula or method used. It must be borne in mind that the stirring is far heavier and more vigorous for this process than for any ordinary class of colour. In the actual colour striking process the stirring must also be very efficient owing to the insolubility of the basic chloride.

In basic chloride chrome making, it is usual to employ hydrochloric acid or sulphuric acid to neutralise the caustic soda produced by the interaction of the lead oxide and sodium chloride.

These processes require to be worked out and established on a successful basis by the manufacturer himself. For this reason, only brief details of the preparation of the oxychloride and the quantities of ingredients for the pigments are given here. In making the lemon and middle shade, great care must be exercised to ensure that the batch is kept acid throughout, and finished distinctly acid, prior to washing and drying.

Preparation of Basic Lead Chloride for Lemon Chrome. 600 lbs powdered litharge are stirred into 200 gallons of water; then 125 lbs. salt (NaCl) are added. This mixture is thoroughly beaten up at 30° C. by vigorous stirring until no trace of free litharge is left When that stage is reached, the mixture is *slowly* "thinned out" by running in 300 gallons of water. The water must not be added too rapidly or some hydrate may be produced. *The next stage is to add part of the first sodium chromate* (175 lbs. $Na_2Cr_2O_7.2H_2O$) run in as a 20 per cent solution, while stirring vigorously. The precipitate so formed is washed once and the top liquor run off. The batch is proceeded with by slowly running in 80 lbs. sulphuric acid in 20 gallons of water, with good stirring. To finish the batch, a further 90 lbs. of the bichromate as a 10 per cent solution containing 45 lbs. of sulphuric acid is added. This leaves the batch quite acid and with a fairly high content of soluble salts It is therefore necessary to stir well and allow to settle properly each time the batch is washed up Too much residual saline matter will give a hard product on drying.

Basic Chloride Middle Chrome. In this case the procedure is just the same, except that sulphuric acid cannot be used to neutralise alkalinity as lead sulphate would be formed and the shade be much too pale. Hydrochloric acid is therefore used. Appropriate quantities are

Litharge	800 lbs.
Salt (NaCl)	160 ,,
First bichromate ($Na_2Cr_2O_7$ $2H_2O$)	245 ,,

Wash up and run off the top liquor, then :

Hydrochloric acid (28° Tw)	160 lbs
Water	40 gallons

And finally .

Additional sodium bichromate	260 lbs
Hydrochloric acid (28° Tw)	240 ,,
Water	200 gallons

Orange and Red Chromes Orange and red chromes are essentially different from the other three shades Being basic in character, there is less risk of their changing in colour during drying. They are struck in boiling solutions, and concentrations up to 25 per cent are employed.

A typical formula for "acetate" orange chrome is given below.

2 cwts. litharge are suspended in 80 gallons of boiling water in a 350-gallon vat.

54 lbs. of 80 per cent acetic acid are slowly stirred in and the boiling is continued.

84 lbs normal sodium chromate are dissolved in 80 gallons of hot water and half of this is run in *rapidly* while the basic lead salt suspension is maintained at 95° C Agitation should be slow, the main mixing being brought about by boiling with "open" steam. The remaining half of the sodium chromate is added more slowly, about 2 gallons at a time, the total time of addition of the chromate being about two hours. The boiling is continued for a short time, and the product washed and dried in the usual way

A deep rich shade, of good texture, is made as follows .—

Pulp white lead (ground in water) equivalent to	1 cwt. dry white lead
is suspended in—	
Water .	60 gallons
and then—	
Lead nitrate	60 lbs.
in	
Hot water	40 gallons
run in	

This mixture is agitated and brought to the boil, then :

Normal sodium chromate	54 lbs

are added in the same way as for the "acetate" orange chrome above

This formula gives a richer, deeper shade, and good opacity and texture

A cheaper method is to dispense with the use of lead nitrate, proceeding as follows .—

To the hot suspension of pulp white lead equivalent to 1 cwt. dry, run in a mixture of :

Sodium bichromate .	52 lbs	in 50 gallons hot water.
Caustic soda (solid)	30 ,,	

Boil this mixture till the desired shade is obtained. This will take about 15 minutes An orange to red shade is produced, strong and of good opacity, but not quite so bright or soft in texture as the preceding one

Another method, by which a "scarlet" chrome is obtained, is as follows :—

Lead acetate	2 cwts	A.
Hot water	100 gallons	
Normal potassium chromate	77 lbs	B.
Hot water	100 gallons	
Caustic soda (100%)	30 lbs	C.
Hot water	20 gallons	

Solution B is run into A, at a moderate speed, with good stirring, then allowed to stand one hour and the top liquor run off as far as possible. C is then run in rapidly with good stirring and the mixture boiled with "open" steam for 15 minutes The colour must be thoroughly washed before drying. A bright shade and a soft product are thus obtained.

Zinc Chromates

Chromate of zinc, although it is not quite insoluble in water is extensively used as a pigment, owing to its pale bright colour, and its permanence to light and to lime. H. Wagner (Die Korperfarben, 1928, page 123) gives formulæ which indicate that the pigment is hydrated zinc chromate combined with potassium chromate. There are two methods of making this colour—(*a*) by acting on a suspension of zinc oxide in zinc sulphate solution, with potassium bichromate, at high concentration, (*b*) the same process as (*a*), but using sodium bichromate in place of the potassium salt Method (*b*) yields a product which is not quite so pale a greenish-yellow and is more soluble in water than that made by process (*a*). For that reason the potassium salt is invariably used. The sodium salt is only employed when it is essential to keep the price as low as possible, irrespective of quality.

A usual method of procedure is to make about half a ton in a 600-gallon vat provided with good strong stirrers, capable of heavy duty The zinc oxide is suspended in water and zinc sulphate crystals charged into the mixture while stirring. When all is dissolved and uniform, the *solid* bichromate is slowly worked in, keeping the stirring going all the time. All materials and solutions are kept as near 16° C as possible, and after half an hour's further stirring, the batch is allowed to stand for some hours, then filtered direct, without washing This is contrary to methods given in some of the old textbooks, in which a system of graduated washing, with a storage system for saturated wash liquors, is described Such a process is very seldom used to-day The actual filtering is done in fairly thin layers on a good vacuum filter and the filter cakes are then *screw-pressed* If the zinc yellow be required for special work and if the price warrants it, the press cakes may be again "puddled up" with about twenty or thirty gallons of water and re-pressed. The press-liquors are not usually kept, unless for adding to fresh batches of cheaper grades If sodium bichromate is used, the temperature at the end of the reaction, and *during pressing*, must not fall below 16° C, or Glauber's salt, which becomes much less soluble below that temperature, will crystallise out. This danger does not arise when using potassium bichromate, as potassium sulphate is much more soluble

A typical formula is as follows —

Zinc oxide (red seal)	800 lbs
suspended in—	
Water (15° C)	200 gallons

and churned up to a smooth paste, then "thinned" with a further 150 gallons of water

Zinc sulphate crystals	240 lbs

are then added and the mixture stirred for half an hour. Over the next half hour 200 lbs. of the solid potassium bichromate are added. The final temperature should be about 17° C and may fall to 15° C before filtering The batch may be made slightly more concentrated if desired.

In place of zinc sulphate crystals, a cheaper process is to use the equivalent amount of extra zinc oxide, in making the wet zinc oxide paste, and add the required amount of sulphuric acid in the 150 gallons of additional water when "thinning" the paste prior to the addition of the bichromate. In either case very intensive stirring is an essential feature of the process if a soft light product of good shade be desired.

The pressed colour cakes are dried at a very low temperature, *preferably in a vacuum oven.* The soft lumps partly fall to powder and the product is sold in that condition, or it may be lightly crushed between the rollers of a granite roller paint mill.

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CHAPTER IX

CYANIDE BLUES

THE term "iron blue" covers a number of types and shades of "Prussian blues" which vary in shade, undertone, and general properties. These various blues are known under the names "Prussian blue," "Chinese blue," "Milori blue," "Bronze blue," "non-bronzing Prussian blue," "Gas blue" Unfortunately these designations have become somewhat confused, although they should refer to very distinct individual types.

A Milori of Paris was the first continental maker to produce a really bright clean blue successfully on a commercial scale, and the name "Milori blue" owes its origin to that fact. Prussian blues were also made in England by the Cornbrook Chemical Co., at the same period. Milori or Chinese blues are really almost synonymous terms and refer to the bright strong shades with a pure greenish-blue undertone The original Milori blues showed a moderately bronzy appearance in oil, whereas the best grades of Chinese blue are assumed to be as free from this bronzy appearance as possible, and to have a pure bright greenish-blue undertone "Prussian blue" apart from being a generic term, usually refers to the same type as a pure "bronze" blue, i e., both are strong, deep shades with a reddish or violet-blue undertone The best grades of Prussian blue of full reddish undertone, contain small percentages of alumina, due to their being struck in potash alum solution, and are almost devoid of bronziness.

"Gas blue" is the special Prussian blue manufactured direct from the cyanide liquors by the large coal gas undertakings. Being made by cheap direct processes from what are really by-product liquors, they form the cheapest grades of Prussian blues Generally speaking they are of excellent quality, but vary rather in strength and shade. As a rule they do not show excessive bronziness. They have a greenish undertone and a rather flatter, duller shade than the blues struck in the pigment works.

Other types of iron blues are the well-known Celestial or Brunswick blues, these terms being synonymous. The cheaper, weak varieties of Brunswick blues are produced by grinding a suitable base, such as barytes, with a full strength blue of greenish undertone. This method gives a cheap, easily produced product, if carried out in a big heavy grinding mill. The brightest greenest shades can only be produced in the "wet way," i.e , by mixing the necessary base or extender, such as blanc fixe or barytes, with the prussiate of soda solution and then precipitating the blue direct on to the base. This yields very bright clean shades of Celestial blue, especially on blanc fixe. The blanc fixe may alternatively be precipitated simultaneously with the blue, but this is not usually done, and probably gives too green a shade for most purposes

However, most commercial grades of reduced blues (Celestial blues) are made to-day by dry grinding strong blues with the extender, in a heavy edge-runner mill. This has been made possible owing to the great improvements which have taken place in modern heavy grinding plant, and by the fact that pure blues of bright greenish undertone can be produced with far greater certainty by present-day manufacturers.

For general use in paints, enamels and cellulose, there is a great demand for Prussian blues which are free from bronziness in oil. The exact conditions governing the production of Prussian blues of uniform quality in successive batches appear to be shrouded in mystery. The main factors are physical and depend almost entirely on four things

1. Principally, the type of oxidising agent used to oxidise the blue
2. The rate of addition of all ingredients and especially of the oxidising agent
3 The dilution, temperature, rate of stirring and other physical conditions, such as duration of "standing" between striking and oxidising.
4. The use of less oxidising agent than theoretically required, and the introduction of as much atmospheric oxygen as possible in the boiling up, if non-bronzy blues be required.

All these factors must be rigidly controlled, including the initial normal temperature and the rate of boiling up. The best working conditions for any one plant must be determined by actual experiment

The precipitation of a few per cent of alumina in the blue, at the time of striking, will have a considerable effect in preventing bronziness, but will give a blue of a paler, flatter shade in oil. To obtain consistent batches of the pure deep shade, free from bronzy appearance, is most difficult, and some makers rely entirely on selecting occasional good batches, which are put on one side for sale as non-bronzing blue

The only definite rules which can be given as a sound guide in making non-bronzing blues are .

1. Use only potassium chlorate and hydrochloric acid as the oxidising agent.
2. Introduce the main oxidising agent (the potassium chlorate) into the prussiate solution *before striking* the unoxidised blue.
3. Take care to use a slight deficiency of oxidising agent, so that the final depth of shade is produced by air oxidation during washing and drying.
4. Do not add the oxidising agent in a concentrated form, but add it slowly in small quantities as the reaction proceeds.
5. Keep the solutions slightly weaker than for bronzy blues, i.e., 8 per cent to 9 per cent concentrations instead of the usual 10 per cent strength.
6. Stir very thoroughly throughout the whole process
7. If the blue be made rather weaker in strength, as, for instance, by the inclusion of aluminium oxide, a non-bronzing blue is more readily obtained
8. If the pigment has to be dried, drying should be conducted rapidly at a low temperature.
9. Do not oxidise the blue at too near the boiling point.

General rules governing the manufacture of other types are quite definite and include the following :—

Prussian Blues of deep shade, full reddish undertone and only moderate bronziness, are struck in a solution of potash alum.

The following is a typical formula, made at the customary 10 per cent concentrations —

Clean green copperas 120 lbs.
are dissolved in a wide 1,000 gallon vat in—
Water (cold) . . 120 gallons

Potash alum 200 lbs.
dissolved in—
Water . 100 gallons
is run in, while stirring As soon as these two solutions are well mixed—

Yellow prussiate of *potash* 100 lbs.
dissolved in—
Water .. . 200 gallons
is slowly added

All these solutions should be at 16° C. or as near that as possible. The potash alum is essential for the production of a rich violet blue undertone

The oxidation is effected by means of 6 lbs of potassium chlorate, run into the solution, followed by 50 lbs of commercial nitric acid, added slowly over a period of 1 hour. The boiling is usually continued for 4 to 6 hours in making this reddish shade

The washing must be done by settling out as far as possible before the first run-off. Further washing should only be continued to a reasonable point, for with excessive washing a very undesirable semi-soluble or ultra fine form of blue will be obtained, which is most difficult to filter, and will float badly in any oil paints in which it may be used later

Should a batch of blue be overwashed and tend to become "soluble" or refuse to settle, the trouble may be to a large extent rectified by the addition of a little dilute acetic acid to the washed batch

Batches of blues required quickly for cheaper work may be washed rather more quickly by using soda carbonate to *partly* neutralise the excess acid in the batch, after the first washing. Care must be taken in doing this to use the alkali in solution, and to add it slowly, while stirring. Some excess mineral acid must be left in the batch at this stage.

All blues of this type must be dried in a good current of hot air at a fairly low temperature, otherwise the shade will be spoiled and the pigments may fire if dried at too high a temperature. Firing is much more likely to occur if the oxidising agent has been used too liberally

Bronze Blue A good deep pure shade of bronze blue can be made by the following method :—

A	Prussiate of potash Water	200 lbs 200 gallons	at 16° C.
B	Clean green copperas Water	210 lbs 200 gallons	at 16° C.

are run simultaneously into a 2,000-gallon vat in which the agitator is kept stirring. After ten minutes' mixing add :—

C.	Hydrochloric acid (28° Tw.)	300 lbs

The mixture is stirred and boiled for 1 hour, after which a solution of 26 lbs potassium bichromate in 50 gallons of water is slowly added, over a period of about ½ hour. The blue is further boiled for 1 to 2 hours, and finally allowed to settle down well before being run-off and washed.

The slow addition of the oxidising agent is necessary to avoid a weak flat tone.

Potassium bichromate is used as it gives the best bronzy appearance.

Chinese Blue. This is made by the same general method as Bronze blue, but all solutions should be quite cold, 12° to 14° C. if possible. The oxidising agent is run in slowly, and the mixture brought to the boil before adding the hydrochloric acid to decompose the chlorate. The so-called "boiling" is preferably at a temperature of 90° to 95° C. and continued for 5 or 6 hours. The solutions suitable are as follows :—

A	Prussiate of potash	205 lbs
	Water	200 gallons
B.	Green copperas (must be clean and fresh)	200 lbs
	Water	200 gallons

These are run together into a 2,000- to 3,000-gallon striking vat and "C" then run in—

C	Potassium chlorate	13 lbs.
	Water	15 gallons

After stirring 10 minutes, the temperature is raised to 90° C. and "D" run in over a period of 1 hour.

D	Hydrochloric acid (28° Tw.)	200 lbs.
	Water	25 gallons

The temperature is raised to 95° C. and held there, stirring the batch continuously for a further 4 to 5 hours.

This method gives a bright greenish-blue undertone and usually very little bronziness.

Prussiate of Soda Blues. All the preceding blues have been shown as made with prussiate of potash, which is generally used for the highest priced colours. The cheaper prussiate of soda, which was first made by some of the German gas works, affords a means of producing cheaper blues The results obtained, however, merely by replacing the prussiate of potash with its equivalent of prussiate of soda are unsatisfactory, only very pale flat shades being obtained. It has been found, however, that really good "soda blues" can be made by the use of potassium and ammonium salts in the solutions. The ammonium compound appears to be indispensable, but the potassium salt can be confined to the use of potassium chlorate as the oxidising agent. It is more usual also to employ some potassium chloride in the solutions before striking the undeveloped blue

A typical formula is given below ·

A	Prussiate of soda	300 lbs
	Potassium chloride	56 ,,
	Water	300 gallons
B	Green copperas	260 lbs
	Ammonium chloride	20 ,,
	Water	300 gallons
C.	Potassium chlorate	15½ lbs
	Water .	20 gallons
D.	Hydrochloric acid (28° Tw)	30 lbs
	Water	20 gallons

This formula gives a fairly bronzy top-tone. The method of working the formula is the same as that given for Chinese blue.

Prussian Blues for Shading If it be desired to use strong Prussian blues for shading or tinting greens during the dry grinding and developing processes, it must be remembered that nothing with the slightest bronzy cast or reddish undertone will be suitable. When possible, a weaker Celestial blue type, with bright, greenish undertone should be used Alternatively a special blue may be made and kept for the purpose The most suitable is Prussian blue, struck by the formula given for Chinese blue, with 20 per cent of blanc fixe and 5 per cent alumina in pulp, added before the colour is struck This gives a fairly deep shade, very suitable for tinting work and incidentally very useful as a deep blue for enamel and cellulose work. It is quite free from bronziness and has a good bright undertone Its special suitability for enamels and cellulose lies in the fact that it is quite free from bronzy appearance and that it is much easier to grind than pure Prussian blue.

Pulp Blues Special qualities of blue in pulp form are required for paper staining, for which purpose they are used in very large quantities The qualities most needed are those with a bright greenish undertone. The principal requirements are fine subdivision and good staining power, the latter quality being mainly dependent on the former. These pulp blues must be washed very thoroughly, therefore the chief difficulty, once the desired shade is obtained, arises in the settling out and filtering of supplies quickly enough to cope with the demand The only possible method of filtering for pulp blues, or for those to be dried and ground, is by gravitation into a filter-press. The cloths must be carefully chosen, and must be kept well cleaned between operations and only used fully soaked for starting a fresh filtration The optimum filter head will be found by actual trial, usually between 10 ft and 18 ft clear above the press

Pulp blues are generally used for staining paper during the making of the paper pulp and, therefore, are required as smooth uniform pastes and must be free from mineral acids. Where a large output of pulp blue is required, filtration of the washed blue may be accelerated by slightly salting the last washings with brine (using up to 2 per cent sodium chloride on the total bulk of the blue and wash water).

So called " soluble " blues are sometimes advocated for this important operation of paper staining. This is scarcely necessary, however, for a charge of 1 cwt of wet pulp blue will be churned up in the paper beaters with several thousand gallons of water and will disperse to a colloidal form by virtue of this high dilution.

Blues produced in pulp form for conversion into Chrome greens are sometimes transferred to a " stock " vat and measured off from that as required. This practice is not at all advisable. The best greens in brightness of shade, stability and freedom from " floating " in oil, are made by using the freshly washed blue as soon as possible Storage of the blue tends to alter the particle size and form, to the ultimate detriment of the green made from it.

In washing these blues, excessive washing must be avoided. The final washing must be faintly acid to the very sensitive glazed litmus papers.

A further test often used is to treat a small sample of the top liquor with barium chloride solution. Only a faint turbidity should be produced in the final wash-liquor All blues prepared for the striking of Chrome greens should be tested in this way, otherwise shades may vary considerably owing to the excess sulphates. The special considerations to be observed in making blue for greens are briefly referred to in the next chapter on "Chromate Greens"

Antwerp Blue This is one of the older types of iron blues and is really a combination of zinc and iron ferro-prussiate It gives a good opaque type of light blue, with very little tendency to "float" in oil, but it is not very largely used. A typical method of manufacture is given below :

Zinc sulphate crystals	30 lbs.
are dissolved in—	
Water	40 gallons

Into this solution is run a solution of—

Green copperas	56 lbs.
dissolved in—	
Water	50 gallons
After mixing is added—	
Prussiate of potash	112 lbs.
Water	100 gallons
and finally, a solution of—	
Potash alum	42 lbs.
in	
Water	40 gallons
is stirred in	

The batch is stirred at 40° C. and blown with air for several hours. After settling out and well washing, the colour is filtered, thinly spread out on trays, and dried at a low temperature No oxidising agent is added as a rule, oxidation being entirely effected by the air during washing, blowing and low temperature drying.

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CHAPTER X

CHROMATE GREENS

LEAD CHROME GREENS

THESE are in a class by themselves owing to the fact that the total production of these colours, in various shades and strengths, far exceeds that of any other shade or type The fact that these combined pigments have excellent weather-resisting properties and are very fast to light when properly made, accounts for their widespread use for general decorating work. They are comparatively low in price and of good covering power. At the same time the *pure* pigments are of soft texture and admirably suited for the manufacture of ready mixed paints and enamels, for which purpose freedom from harshness or grittiness is important There would be little need for other green pigments in this range of shades, if it were not for the fact that these greens are not fast to free lime, nor to sulphuretted hydrogen

Chrome greens consist essentially of lead chromate and Prussian blue For the pure bright shades it is necessary that the yellow component should be of a bright lemon shade, rather than a middle chrome yellow It is therefore obvious that some lead sulphate must be present in the finished Chrome green When making full strength rich shades, generally the aim is to keep the lead chromate of the correct greenish-yellow type, with a minimum of lead sulphate, otherwise the finished greens will be weak and flat, or even milky in appearance when ground in oil. Pure rich greens containing the maximum of lead chromate and Prussian blue in proportion according to the shade, are usually termed "C.P." Chrome greens in America and "pure" Chrome greens in this country. Strictly speaking these terms should only be used to designate this type The term "Brunswick green" usually means a lead chromate—Prussian blue type of green, on a base or substratum The term is not exclusively used in that sense, however, but is used by some for the full strength greens.

As described on page 129 only a certain shade and type of Prussian blue can be used for making Chrome greens It must have no bronziness whatever and nothing approaching a reddish- or violet-blue undertone ; only a bright greenish-blue undertone is permissible in the blue to be used Other important points are

1 That the blue should be well washed, without over-washing, and used freshly made rather than kept in stock ready made.

2. The whole of the lead solution or suspension for the yellow chrome component should be added to the blue and stirred well in, before any of the bichromate is added. The reason for this is that a large proportion of the soluble lead is definitely adsorbed by the Prussian blue particles, and therefore there is a much more intimate association between the blue and yellow components in the finished product.

3 As in making the Chrome yellow, the bicrhomate and sulphate solution is added fairly slowly with good stirring.

4 Where tartaric acid is used to keep the brightness of the greens unimpaired in washing and drying, it must be added to the finished green immediately the whole of the bichromate solution is stirred in, otherwise it is far less effective The tartaric acid solutions for this purpose must therefore be prepared in advance and placed ready for use Most writers have stated that the action of tartaric acid in this connection is a mystery, and this appears to be the safest view to take at present The only other common substances which are of use in the same way, but to a lesser degree, are small quantities of *glue*, *Turkey red oil*, *ammonium phosphate*, and in some cases *acetic acid.* Acetic acid, in common with other organic acids, is not at all reliable as a brightening agent for greens, and this fact makes the action of tartaric acid even more difficult to explain

5. It is generally accepted that a larger excess of lead over bichromate and sulphate is necessary in making a green than in making a Chrome yellow This rule should be interpreted chiefly to mean *local* excesses. In other words the stirring must be rapid, and the bichromate added fairly slowly. A better plan for guarding against too much local excess of bichromate during the addition, is to run this solution in from a good height through a pipe with several branches, so that

the actual addition takes place at four or five points round the vat A good fall on this pipe ensures that the bichromate solution penetrates well into the bulk of the mixture in the striking vat

These five points, if carefully followed out or adapted to the individual process, will be of great help in ensuring bright and stable colours, provided, of course, a well-tried formula is always employed and all physical conditions are kept as near to a standard as possible One of the most difficult problems, particularly with deep bluish-greens, is that known as "floating" in oil. Where the proportion of lead is greater, i e , in yellower shades, this tendency is far less, owing to the "physical affinity" which appears to exist between the wet Prussian blue and the lead solution, when these are mixed ready for the striking of the green. There are two ways in which this difficulty may be minimised (1) By avoiding overwashing both the blue and the finished green, and if necessary giving a final washing to the filter cakes on the filter-press. (2) Using the bichromate solution rather weaker than when making the corresponding Chrome yellow shade and stirring very fast while striking the colour

A very useful general survey of the manufacture of Chrome greens is given in the "Paint, Oil and Chemical Review" July 7th, 1927, p. 8, by D Davidson. This article only deals with one method and with few exceptions this method is the one used by all large scale makers, as far as general procedure is concerned The formula given by Davidson prescribes the use of white lead and nitric acid, which gives greens that are slightly denser than those made by other processes, on the other hand the cost of production is slightly higher than when using the alternative method employing litharge and acetic acid for the soluble lead component. This latter method, if carried out with care, yields Chrome greens rather brighter in shade, and of excellent general properties, such as stability, softness, and moderate oil absorption Also they are not too prone to settle out when ground up in paints The nitrate pure greens are of special utility in cellulose enamels for which they are to be preferred to the acetate type

There are numerous possible formulæ for Chrome greens, but as the individual maker will need to work out his own quantities and conditions of production in accordance with the shades and special properties desired, only two typical green formulæ are given here with suitable working details

Deep Chrome Green (*Acetate*) Using freshly made and fully washed Prussian blue (see page 129 for most suitable method), and litharge and acetic acid for the lead component, proceed as follows

Prussian blue of a suitable bright greenish shade, equivalent to 3 cwts dry blue, is allowed to settle well down after the last washing and the top liquor run off, leaving the blue as a suspension of as near to 6 per cent strength as possible. Once a workable concentration of washed blue is arrived at, this should be exactly adhered to for every batch It is often an advantage to conduct this washing in a tall shaped vat to ensure good settling

500 lbs. of litharge are stirred into 300 gallons of water and dissolved by the addition of 135 lbs. of 80 per cent acetic acid, stirring well until the reaction is quite complete This lead solution is run into the above mentioned suspension of 3 cwts of Prussian blue, and well stirred in. After 10 minutes' stirring, the following precipitating solution is run in at moderate speed

Sodium bichromate crystals	310 lbs
Potash alum	18 lbs.
Water	350 gallons

During this addition, which is made more gradually towards the end, the stirring in the " striking " vat must be as efficient as possible When all the bichromate solution is run in, a pause of not more than one minute is necessary for complete intermixing of the contents of the vat, after which ·

Tartaric acid	10 lbs
in—	
Water	10 gallons

must be immediately poured in

After stirring for 15 minutes, the vat is slowly filled up with water. The pigment is allowed to settle, and then washed until the top liquor is almost free from saline matter As the saline impurities are mostly sodium acetate, the determination of the best point at which to filter is best made by tasting a spot of the later wash liquors. The filling up with water at each washing should be done fairly slowly, and the final washing not carried too far, because if the washing water be too violently dashed into the batch, or if the washing be excessive, partial floating of the blue will occur, and the settling and filtering will be retarded If this should occur, it may be partly remedied by very slowly adding concentrated brine (sodium chloride solution 25 per cent) while stirring, using not more than 20 gallons per 1,000-gallon batch as a maximum

Pale Chrome Green (Acetate Type). The general method of manufacture is the same as for the preceding formula, but the risk of " floating " of the blue is less if good stirring is provided. In this, as in all Chrome green formulæ, some alum is an essential ingredient to ensure that the yellow chrome is precipitated in a bright, clean finely-divided form. The method of preparation of the blue, and other ingredients, and the type of plant used, are the same for the light and middle shades of lead Chrome green as for the deep shade which has been described, except that for the light shade, Prussian blue equivalent to about 90 lbs pure dry blue should be used in place of the 3 cwts taken for a full deep shade, in the size of batch already given The washing of the yellower shades of Chrome greens is more rapidly accomplished than that of the bluer shades, because they settle much better than those having a large proportion of blue

Emerald Tinted Greens. These are usually pale bright shades of Chrome greens, of bluish shade and with a characteristic chalky or milky appearance in oil, due to the china clay base on which they are struck. There is only a moderate demand for this type of Chrome green The shade must be bright, therefore it is usual to prepare emerald tint greens from commercially pure lead nitrate or lead acetate crystals , either may be used. A fine clean grade of china clay is used, and this is well stirred with the ready washed blue, or in some cases the blue is struck on to the china clay base For the same reason as in making Chrome greens, the lead solution is stirred with the suspension of the blue for a few minutes, the mixed bichromate-Glauber's salt solution is then run in moderately quickly and immediately followed by tartaric acid, more of this latter reagent being used than in ordinary Chrome greens A considerable excess of lead is also desirable in this process The pigment must be very well washed.

Suitable quantities for a batch of an average shade of Emerald tinted green are as follows .—

A	Freshly washed Prussian blue in the form of a 5% suspension, equivalent to .	84 lbs. 100%
	China clay . ..	2 cwts.
B	Lead nitrate crystals	172 lbs
	Water	120 gallons
	(dissolved and cooled to 16° C)	
C.	Sodium bichromate crystals	75 lbs.
	Potash alum .	2 lbs
	Glauber's salt crystals	4 lbs
	Water (16° C.) .	100 gallons
	Finally—	
D.	Tartaric acid .	4 lbs.
	Water .	4 gallons

The above quantity can be made and washed conveniently in a 600-gallon to 800-gallon vat.

(2) *Dry Mixing.* Lead Chrome greens are never made by mixing wet suspensions of ready-made blue and ready-made yellow ; the method is quite unsatisfactory Some of the yellower shades may be, and occasionally are, made by grinding a suitable dry blue and yellow together in an efficient modern edge-runner mill This is not often done in the case of full strength colours, but is quite a usual method for making weak strengths of reduced Chrome greens With heavy modern mills the results are very good, and some makers prepare all their cheap reduced greens by grinding the dry blue and yellow with the requisite amount of base until completely incorporated. Exceptions are deep and extra deep shades containing large proportions of blue, these are always made by wet precipitation, as they cannot be satisfactorily incorporated by the dry grinding method

Dry grinding is also used as a means of producing a number of varying strengths of Chrome greens when good quality colours slightly reduced by blanc fixe, etc., are required. Such a standard range of strengths to suit various prices and uses are now invariably made by striking the concentrated greens, and " developing " in a pan mill with blanc fixe or other base

Generally speaking, greens produced by pan mill mixing have a good bright rich appearance, and if a heavy mill with revolving pan and fixed rollers, as described on page 51, be used, the results can scarcely be equalled by wet precipitation of the reduced greens. The "dry" process is of course far more economical than the special wet precipitation of all individual shades and strengths.

The process of wet precipitation of the lead chromate on to a mixture of the base and the blue, for the production of reduced Chrome greens, or Brunswick greens, was quite general until the great improvements in grinding plant enabled colour makers to produce the same colours more cheaply and reliably, and to-day the direct wet precipitation of reduced Chrome greens is very little used by the larger makers Two typical examples are given to illustrate the composition of the usual type of 50 per cent reduced greens

Light Brunswick Green. Prussian blue (see page 129) as a 6 per cent suspension equivalent to 42 lbs. of dry blue is stirred in a vat with 8 cwts of fine white barytes, or mixed barytes and blanc fixe To this mixture is added .

Lead acetate		280 lbs
	dissolved in—	
Water		150 gallons

After stirring for 10 minutes the following mixed bichromate solution is run in

Sodium bichromate crystals	84 lbs
Glauber's salt	18 lbs
Water	100 gallons

The addition is made slowly with good stirring and 4 lbs tartaric acid are added immediately after Owing to the better settling of the blue due to the base, the pigment may be washed quite rapidly as compared with the concentrated greens.

Extra Deep Brunswick Green Prussian blue (see page 129) equivalent to 170 lbs of dry blue is mixed with 9 cwts of suitable base, and the process continued exactly as for pale Brunswick green using the same weights of components for the yellow, except that the 18 lbs of Glauber's salt is replaced by 12 lbs of alum When all the bichromate solution is added, 4 lbs tartaric acid in 10 per cent solution is at once run in The washing is carried out more carefully and slowly than with the light green in order to avoid undue floating.

An older method of making reduced Brunswick greens of weak qualities was as follows

Solution A The barytes or other base was stirred with water and a solution of ferrous sulphate added; next a solution of lead acetate was run in and stirred Lead sulphate was thus produced, with ferrous acetate and excess lead acetate in solution. A solution of prussiate of potash and potassium bichromate was then stirred in The green was thus produced, with its blue component only partly oxidised. The completion of the oxidation occurred during the washing and drying.

Suitable quantities for a weak (30 per cent) middle Brunswick green, by this process are

½ ton of base is suspended in 200 gallons of water Into this run 24 lbs. ferrous sulphate dissolved in 20 gallons water When this is stirred in, add 200 lbs lead acetate, dissolved in 100 gallons water Finally run in the precipitating solution as under ·

Potassium bichromate	68 lbs
Yellow prussiate of potash	24 lbs
Water	100 gallons

2 to 4 lbs of tartaric acid may be added to brighten the shade

This colour is acid when struck. The washing is continued until the last wash water is still faintly acid to litmus

ZINC GREENS

The greens corresponding to lead Chrome greens made from Zinc chrome and Prussian blue are distinctly brighter than the lead greens, but have less opacity and higher oil absorption Although these colours are not fast to free lime, owing to their Prussian blue content, they are of good fastness to light and are therefore used for paints and flat enamels, which are specified as lead-free for use in hospitals, etc , or in localities where the presence of sulphuretted hydrogen in the atmosphere prevents the use of Lead greens Their use was much more extensive before the appearance on the market of bright fast yellows, such as Hansa yellow 3G and 5G , and pyrazolone colours, such as the A G F A Permanent yellow R , and the lighter shades of the series made by J W Leitch & Co. Several of these types of colours are available in bright greenish-yellow shades, at a sufficiently low price to enable the preparation of fast greens as bright in shade as the best Zinc greens, with about the same fastness to light, and with better fastness to water. The blue component for these fast bright greens is usually a strong, bright ultra-blue of full greenish tone, such as the best grades used for lithographic work The two components are ground together in an edge-runner mill with zinc white or other suitable base until fully incorporated.

Hansa yellow 5G. and J. W Leitch's Light yellow 5GL yield very bright greens of good permanence. These greens are fast to lime and are to be preferred to Zinc greens for use in varnish paints or enamels, especially in the yellower shades, as Zinc chrome and Zinc greens tend to form very shiny, "stodgy" enamels of poor brushing qualities when ground in most types of varnishes The greens from greenish shades of ultra-blue and the light yellows mentioned above have no such defect.

Zinc greens proper can best be made by a simple and reliable wet method No attempt should be made to strike the two components at once, for they are better prepared separately, and subsequently mixed. The Zinc chrome is specifically light as compared with Lead chrome, and if it be made with very fast and intensive stirring of the batch, it will be flocculent, light and well subdivided To such a suspension of Zinc yellow, kept rapidly stirred, a calculated quantity of Prussian blue is added This blue should be freshly made and well washed, and have *as bright and greenish an undertone as possible* For the manufacture of deep bluish shades of Zinc green, not more than 6 parts of Prussian blue (calculated as dry blue) to 100 parts of Zinc yellow (calculated as dry yellow) will be required It will be seen that these greens consist almost entirely of Zinc chrome, and actually they have most of the defects of Zinc yellow, with the added lack of fastness to lime of the Prussian blue When making rich middle and deep shades, the Zinc yellow should be made with less excess zinc oxide in the formula than when making standard Zinc chrome, otherwise the shades will be rather flat and milky.

CHAPTER XI

Other Precipitated Metallic Pigments

FERRITE YELLOWS

THIS chapter deals chiefly with less commonly made and used metallic pigments, although this description scarcely fits the Ferrite yellows They are special synthetic grades of ferric hydrates made by a continuous process, covered by American patents (U S.P 1,368,748 and U S P. 1,327,061)

The process and plant is fully described in E P 153,792. The main essentials are that a ferrous salt, such as ferrous sulphate, is placed in a wooden vat in contact with free metallic iron and the mixture kept boiling while air is constantly blown through the solution As a result, a ferric iron salt is produced and ferric hydrate is precipitated. The ferric salt reacts with the free iron to form ferrous salt again (making three molecules of ferrous salt from two of ferric salt) In this way the cycle recommences and the only materials required to be renewed during the process are iron, water, and oxygen The colour is thus virtually produced from scrap iron, air, and water (steam). The shades are modified by changes in concentration and other working details, physical changes being mainly responsible

The products have an extremely fine soft texture and great density (about three times the strength of ordinary strong ochres). The shades are from that of the palest yellow ochre to that of a clean, rich, raw sienna, the Ferrite yellow shades being brighter than those of any natural earths of similar shade. The only disadvantage under some circumstances is the very high oil absorption of these synthetic pigments. Being so soft and fine, and of good yellow undertone, they are much to be preferred to natural ochres for all tinting down of white enamels, flat and glossy, and distempers for cream to buff shades.

CADMIUM SULPHIDE

This extremely fast yellow to orange range of pigments includes colours of great opacity and cleanliness of tone They are rather troublesome to manufacture and comparatively expensive. The method of production is to pass sulphuretted hydrogen gas through a solution of cadmium chloride The variation in shade is chiefly brought about by changes in the concentration and other physical conditions, and by the use of some zinc chloride for very pale shades With very weak solutions and a slow precipitation, paler and yellower shades are obtained. The process is carried out in a closed earthenware vessel of exactly the type and shape of a Woulff's bottle. The gas is passed to the bottom of the solution and emerges through fine perforations or slits in the earthenware leading tube. Any excess gas passes through lime scrubbers and eventually to a stack or furnace flue

The cadmium chloride is usually acidified with 2 per cent of its weight of sulphuric acid before blowing in the gas. As the gas is *extremely poisonous* the process can only be carried out by skilled workers in a special plant and lay-out.

ANTIMONY VERMILION

Ingredients	40 lbs	tartar emetic
	26 to 28 „	tartaric acid
	96 „	sodium thiosulphate

(*a*) Dissolve the tartar emetic in 20 gallons water and add the tartaric acid, then

(*b*) Prepare a solution of the sodium thiosulphate in 20 gallons water at 45° C., and add this slowly with good stirring to solution (*a*)

Keep this mixture at a temperature of 50° C. to 60° C., when the Antimony vermilion gradually separates out.

Wash, filter and dry in the usual manner at a low temperature.

The filtrate should be only faintly *acid* The colour is very fast to light, bright and opaque, but only of moderate fastness to heat, and not fast to acids and alkalies. It can, however, be used in hot process vulcanisation of rubber.

A French patent (605,401) claims the production of golden-yellow shades by a similar method in the presence of zinc salts.

EMERALD GREEN

This is mainly composed of copper arsenite and basic copper acetate Specially bright shades of similar composition were originally known as Schweinfurth green They are little used to-day except for high-class decorative and artists' work

The following is a typical formula .

2 cwts. of acetic acid (6 per cent) are stirred in a clean earthenware tank. Into this, 10 lbs. of pure slaked lime are stirred. To this is slowly added a solution of 52 lbs. copper sulphate crystals in 40 gallons water (at 25° C) Finally 48 lbs white arsenic is added with good stirring and then, after stirring 10 minutes, is allowed to stand warm The green slowly crystallises out When crystallisation is complete, run off the liquor, collect and drain the crystals of Emerald green, and then dry them at a low temperature All manipulations must be carried out with great care. In particular, the arsenic must be so handled that there is no possibility of the powder floating in the air.

COBALT BLUE

This is variously prepared as cobalt-alumina-phosphate, e.g , the original Thenard's blue, and more recently as alumina-cobalt basic sulphates

A simple method of preparing the latter type is as follows .—

28 lbs of cobalt acetate and 240 lbs potash alum are dissolved separately and run into a mixing vat To this mixed solution at 20° C. sufficient 10 per cent sodium carbonate solution is added very slowly, until precipitation is just complete. The product is washed and filtered to a hard cake, which is placed in clean porcelain pots and heated in a muffle at a *dull-red* heat for ½ to ¾ hour. The product is finally ground in a granite edge-runner mill

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SECTION 4

PIGMENT DYES

CHAPTER XII

PIGMENT DYESTUFFS AND DYE-COUPLING

PIGMENT DYE MANUFACTURE IN THE LAKE-COLOUR WORKS

FOR various reasons, such as the necessity for producing the dyestuffs in some special form, or the elimination of some minor processes which would add unnecessarily to the cost if the dye were bought in a convenient saleable form, it sometimes pays the pigment manufacturer to make his own dyes and thus eliminate such processes as filtering, drying, powdering and standardising to a given strength. Packing and other charges can also be eliminated Finally there is the case of the pigment works run on such a large scale that it is necessary to produce as much of its own material as possible. Such a works will generally run a branch works or section for dye and intermediate manufacture.

The necessity for this, in the case of certain colours has been long recognised For example, at one time it was considered policy by a few of the larger makers to produce their own naphthol green B and Lithol red dyes These are seldom made by the pigment maker at the present time. The former has been largely displaced by the newer pigment green B, which is of similar shade (though not quite so bluish on reduction as the brightest varieties of naphthol green B), but has the advantages of being much faster to acid and to water, and is equally as good in fastness to light and lime At the same time the dyestuff naphthol green B can now be obtained in such a standard pure grade that it is hardly worth making

Lithol red, again, is a colour presenting many technical difficulties in its manufacture, and can only be made economically on a very large scale It is produced in such quantities by the few dye makers who specialise in its manufacture, that this dyestuff again is hardly worth making in the pigment colour works, so long as it can be bought in such uniform quality so cheaply Quite a number of colour works do still make their own Lithol red dye, and for this reason a few typical working details have been given.

Other dyes which for special reasons, are made in the pigment works are pigment scarlet 3B. (though rarely), Permanent red B ,2B. and 4B , Lake red C , Lake red P., Lake red D. and para (or autol) red Orange II and the ordinary acid Ponceaux are sometimes made, but have not been dealt with in detail in this chapter, as they have been so largely superseded by newer and better dyes

Then again the line of demarcation between dyes and pigments is rather arbitrary, for such pigment dyes as Lake red C can be and are sold as dry *sodium salt* dyestuffs for extra pale scarlet shades of printing ink, and give perfectly satisfactory results. The pigment maker can in this way make a " dye " and sell it as a pigment or lake. On the other hand some dye manufacturers prepare the pure barium or calcium salt of Lake red C., Permanent reds, etc., and sell them as dyes for printing inks

In cases where it appears to be sound economic policy for the lake maker to do some of his own dye-coupling, the fairest arrangement seems to be for the dye maker to co-operate and supply the intermediates, with full margin of profit on the intermediate, in view of the great expense and difficulty of preparing and purifying them

INSOLUBLE PIGMENT DYES

The difficulties connected with insoluble pigment dye manufacture and the need for special precautions are much greater than in making the soluble varieties, and therefore these are dealt with first This chapter is confined to the scarlets and reds, which are the only dyes of this type generally made by the pigment or lake maker

Most of the special difficulties arise from two sources

1. The insolubility of the diazo compounds and the fact that these can only be easily coupled when finely subdivided

2 The fact that the dyestuffs are usually quite insoluble and form a gelatinous coat round any particles of diazo compound which are not sufficiently subdivided

3 The fact is not often recognised that all dyes of this type are formed far more readily in solutions as nearly neutral as possible, and having a minimum saline content in the mixture at the time of coupling

The special precautions which will tend to give uniformity of results and first-class products *in this range of dyes,* are all aimed at overcoming the difficulties set out above They include the following essential points —

1. Intensive and dependable stirring

2 Using as large a bulk of water as possible for a given size of batch

3 (Which is partly dependent on 2) The cutting down to an absolute minimum of soluble saline matter (extraneous to the main dye coupling)

4 The use of a minimum amount of free alkali

5. Constant testing of the batch, by specially suitable methods with the correct type of test papers

6 Coupling at the most suitable temperature, which is in some cases very low and in others as high as 25° C.

Lithol red being the most profitable of all the bright pigment reds, as regards such desirable qualities as strength, price and reasonable fastness to light in full shades, is made in larger quantities than any other pigment red, up to the present time. Its production is so centralised and specialised that, as before mentioned, it will generally be cheaper and better to buy a good standard paste Lithol red ready made.

For those who are interested in its manufacture in the pigment colour works, the following working formula is given in minute detail, as it represents the general method of procedure and shows the general precautions necessary for the successful production of most insoluble pigment dyes of this class.

The diazo compound is prepared in a square section wooden vat to allow very vigorous stirring and beating up. The vat should be of close-grained pitch-pine and not lead-lined. A loose wooden cover is provided to avoid splashing and to facilitate subsequent washing down If possible, this vat should be on the third or even fourth floor The beta-naphthol solution can be made ready in the coupling vat, which should be on the first floor, while the filter-presses are on the ground floor, if the colour is to be pressed by gravitation feed.

This naphthol solution is made as below

Beta-naphthol	72 lbs (100%)
Caustic soda	19 lbs (approx 100%)
Ammonia	2 lbs (880)
Water	350 gallons

The beta-naphthol is stirred into 350 gallons of water in the coupling vat at 20° C. and stirred ½ hour with 19 lbs. of caustic soda After stopping the vat stirrer, it is verified that no solid beta-naphthol remains in the centre at the bottom of the vat by withdrawing some of the solution by means of a long glass tube reaching down to the base of the vat. The alkalinity is then carefully adjusted with small additions of caustic soda until the solution only *just shows* free caustic alkali to Titan yellow papers At this point, the 2 lbs. of ammonia are added and the temperature adjusted to 18° C with a little ice if necessary This solution is then ready to receive the diazo mixture, after a final examination of belts, gears, etc , to ensure that no hitch shall occur in the mixing during the coupling process

The coupling vat is preferably lead-lined so that it can be quickly washed out and used again without detriment for a different shade of pigment red dye

Run 80 gallons of water into the diazo vat, and heat to 25° C Then stir in Tobias acid equivalent to 114 lbs. (100 per cent). Stir this vigorously for 5 minutes to break it up finely Do not add the caustic soda first, or there is a tendency to cake up Now run in caustic soda equivalent to approximately 21 lbs. (100 per cent). The final point is taken by testing with a glazed litmus paper till a distinct trace of free alkali is present Cool with ice and water to 16° C , and keep the bulk at as near 130 gallons as possible. If any decided cloudiness shows at this stage, due to iron compounds or di-naphthyl, the solution should be *filtered* and returned, without loss to the square diazo vat Stir vigorously and *rapidly* run in 130 lbs of hydrochloric acid (iron free) of 28° Tw. strength The mixture will be at about 17° C. and is made to a bulk of 160 gallons, and must be rapidly stirred for 10 minutes to break up the precipitated Tobias acid into the correct form, before adding the sodium nitrite. The nitrite solution consists of 35½ lbs. (100 per cent) sodium nitrite (about 36½ lbs dry crystals) dissolved in 70 lbs of water at 20° C Three-quarters of this solution (at 16° C) is run rapidly into the Tobias acid mixture, which is kept vigorously stirred A pause is then made and the presence of a slight excess of free hydrochloric acid is verified with Benzopurpurine 4B papers (*not Congo Red papers*), which are sensitive to the organic (Tobias) acid As soon as a test with fresh starch-iodide papers shows that the nitrite has been completely utilised, gradual additions of the remaining quarter of the nitrite solution are proceeded with, testing all the time in advance with Benzopurpurine 4B paper to ensure an excess, but *only a slight* excess, of free hydrochloric acid The quantity given above may leave a slight deficit, and if so, as the acidity begins to disappear leaving still some nitrite to add, additions of 1 lb at a time of hydrochloric acid should be made to keep the batch faintly acid until the end. The reaction is completed when sufficient nitrite has been added to show a permanent faint reaction to fresh starch-iodide paper after a lapse of three minutes, stirring, and the acidity is only just enough to show a faint but distinct reaction to Benzopurpurine 4B papers The vigorous stirring is continued for 10 minutes, then slowed down and continued slowly for another 10 minutes The diazo compound is then filtered, preferably by gravitation, in a wooden filter-press with strong woollen cloths, or even in an open box filter It is best left as a stiff uniform paste without any really hard pressing There is no necessity to wash with water, and undue loss will occur if this is done Any attempt to salt out and avoid loss by the addition of sodium chloride, converts the diazo compound into a very unsuitable form and actually increases the loss At the filtering stage, the diazo mixture is at about 18° C and may be cooled with ice to 15° C or 16° C , provided the bulk is not increased to more than 180 gallons It will filter at 17° C to 18° C. if well carried out according to the above details, with not more than 2 per cent loss of the total diazo compound

After being filtered to a uniform cake, the diazo compound is collected and again put in the diazo vat It is there churned up and very gradually " thinned down " with water and finally well beaten up by fast stirring with water (the final bulk is 150 gallons) for ½ hour before coupling It is then in an ideal form for the reaction. Three-quarters of this diazo mixture is run down rapidly (a full 2-in bore with this size batch and a full 3-in. bore with a double sized batch) into the beta-naphthol solution in the coupling vat, stirring the latter all the time at full speed After a short interval the dye mixture is tested as follows it should be strongly alkaline to glazed litmus papers, and should clearly show free diazo compound in the clear rim when spotted on filter paper and tested with beta-naphthol solution Any excessive caustic soda which might be present accidentally can be easily recognised at this stage, for a real excess prevents the coupling from taking place completely When spotting the dye mixture on filter paper a large excess of caustic soda is recognised by the following appearance —

The spot of pasty dye is surrounded by a colourless rim, and after this has spread some distance on the filter paper, the excess caustic soda becomes absorbed and a deep red ring forms right round the clear rim In other words some beta-naphthol and some diazo-compound are both present in the clear rim and are not in a state to couple until some of the excess caustic soda has been absorbed by the filter paper Pure light shades of Lithol red cannot be obtained unless the alkali is well under control.

After verifying the alkalinity and the presence of an appreciable excess of beta-naphthol, the remaining quarter of the diazo mixture is run in, slowly and progressively, meanwhile testing the mixture in the coupling vat from time to time. No great harm is done if a slight excess of either diazo-compound or more excess than usual of beta-naphthol remains at the end of this mixing, provided this is corrected at the time by adjusting with small additions of the one or the other component until a final slight excess of beta-naphthol remains.

At this stage the coupling is never quite complete, the speed of its ultimate completion being dependent on the efficiency and rate of agitation. The last few per cent of diazo compound and beta-naphthol require some little time for the removal of coatings of dye and to become sufficiently dispersed to couple at the low concentration, which these last traces represent in such a bulk A test of the dye mixture should now be distinctly alkaline to glazed litmus paper and a slight excess of beta-naphthol should finally be shown Any considerable excess of beta-naphthol will spoil the form of the dye particles and give a tendency to bleeding An excess of diazo-compound, unless corrected within the first 15 minutes or so of the final addition, will result in its decomposition, giving rise to a dirty shade and undertone, and cause the lakes produced to bleed distinctly in oil

The stirring is continued and the coupling will generally be quite finished after about one hour if the stirring has been vigorous The progress of this final stage can be followed by testing regularly with glazed litmus paper, which will gradually show a weaker alkaline reaction, and if the alkali has been carefully controlled at the beginning, this alkalinity will finally almost disappear. During the coupling, free sodium beta-naphtholate reacts strongly alkaline to the glazed litmus paper ; when it has all combined, only the very slight excess of free alkali in the whole bulk is left to give the reaction Should this alkalinity to the sensitive type of litmus entirely disappear, it must be restored by stirring in successive 1 lb. lots of soda ash (in solution) until it is permanently restored When the coupling is judged to be quite complete, and (if the plant is not well designed for rapid and thorough agitation), this sometimes takes several hours, then a small test sample of the colour must be gently boiled up in the laboratory in a test tube In this test, it is important to verify that the faint alkalinity remains after boiling up. If it does not, or if the dye does not boil up to a pale bright scarlet with a golden-bronze sheen, but during boiling turns to a dull brownish-red flocculent mass or to a greenish-bronze sandy mass. the presence of excess diazo-compound must be assumed Consequently, the large scale boiling up should not under any circumstances be proceeded with until the small test in the laboratory can be heated up to 100° C. without discoloration or loss of free alkali

Most of the troubles with Lithol red batches, such as slowness of completion of the reaction and failure to " boil up " to a bright bronzy form, are due to traces of diazo-compound Fortunately there is a very simple and certain way of detecting this in the colour batch, and this is also the method to use to judge the completeness or otherwise of the coupling.

Take about ½ oz of the dye mixture in a 1-in test tube and pour in 1 oz of 5 per cent acetic acid Shake thoroughly for 2 minutes Then spot this acid mixture on to filter paper and test the clear rim with an alkaline solution of " H " acid. The least trace of diazo-compound will be easily detected in this way and the method should be invariably used for all batches of Lithol red, Lake red C and similar dyes, which are themselves insoluble and made from insoluble diazo-compounds When traces of diazo-compound persist for a very long period and excess beta-naphthol is still present in the mixture, the addition of about 4 lbs 80 per cent acetic acid with 15 minutes' stirring, followed by the addition of sufficient ammonia to render the batch distinctly alkaline to litmus, will put the batch right Any such additions should be diluted with water and added to the batch while stirring. If a batch be started in the morning with diazo-compound made the previous afternoon, and filtered overnight, several hours stirring after the coupling can generally be allowed and still leave time to steam up to convert into the bright bronzy form before night The steaming up is usually done with open steam Stirring should be efficient while this is done and the preliminary heating up to 40° C should be slow From that point the batch may be quickly raised to 80° C, which is usually quite high enough with the conditions and quantities given in this recipe The batch can be left to stand overnight and the next morning after starting the stirrer, when the temperature is at about 50° C, 25 gallons strong brine (20 per cent sodium chloride solution) is very slowly run in to the batch, by syphoning it through a ⅜ in pipe This gives the Lithol red the required form for filtration and for subsequent use The best time for filtering is when the temperature has fallen to 30° or 28° C. The colour can then be easily filtered through a wooden filter press, using a "head" of about 15 ft Press cakes of about 26 per cent or more can be obtained in this way, or more concentrated cakes by subsequent "blowing" with compressed air The full batch of press cakes should be collected, dropped into a small wooden vat fitted with a stirrer and slowly stirred in water to 20 per cent solid content If slowly stirred in this way for 1 hour or more with the addition of not more than 4 lbs Turkey red oil, a fine strong product is obtained owing to the very fine particle size.

When a batch has been made carefully as described, the proper small margins of acid and alkali respectively used, and the bulks and temperatures kept near to those indicated, there is only one variable factor (given pure materials), viz, rate and efficiency of stirring This must be as intensive as possible for quick results and a perfect product The only time when slow stirring is required is after adding the sodium nitrite, just prior to filtering the diazo compound, *in order to avoid froth formation*

The reduction of excess margins of both acid and alkali to the lowest safe limit, ensures a minimum of soluble saline matter in both diazo and coupling stages and is of the greatest importance in each of these stages

The same batch of colour may be quite well made in greater concentrations, but the difficulties of obtaining a well dispersed product and quick, efficient coupling are greatly increased Furthermore at greater concentrations it is almost impossible to obtain the ultra fine dispersion of the final product, which is necessary to give the full strength of the lake (as determined in "reduction tests" with zinc oxide).

The free use of the correct type of test papers throughout as advised in this formula, accurate temperature control, and diazotising and coupling at not below 18° C. all materially help to obtain uniformly good results

Careful testing for final excess of uncoupled diazo- compound by the acetic acid and "H" acid method and its complete elimination before boiling up the main batch, will guard against a batch being spoiled on "boiling up"

If in spite of all precautions, some miscalculation or accident has resulted in too high a content of saline matter or alkali in the final batch, a wise precaution is to filter before boiling up and remix the filter cakes to original bulk with water containing 2 lbs of 880 ammonia, and then again test by boiling up in the laboratory , the main bulk can then invariably be successfully finished. This extra trouble and delay is far better than completing a batch which does not appear to be correct.

When filtering a batch of Lithol red made according to the foregoing details, with the addition of the prescribed amount of brine, and at 30° C., the clear filtrate should be faintly tinged with a clear reddish-pink colour If the filtrate be strongly tinted and of a clear red colour, this may be due to a slight excess of alkali or a slight deficiency of salt. An extra 2 or 3 gallons of brine will correct this. Should the filtrate be of a yellowish or brownish colour this will usually be due to traces of decomposed diazo-compound. Isomerides in the Tobias acid will also cause an unduly coloured filtrate from the dye

For making very cheap strong reds from Lithol red, some manufacturers have used processes in which the dye, after coupling, was not boiled up and filtered In this procedure, as soon as coupling was complete, barytes or other base was stirred in, the batch was then allowed to settle, by which means the dye was carried down along with the base, leaving approximately two-thirds of the clear mother liquor on top. This clear liquor was run off, the vat filled with water, boiled up, and precipitated with barium chloride

This process is a cheap one and gives good, though somewhat darker, duller shades It is not to be recommended for first-class or uniform work, in which case the boiling up of the dye, filtration, mixing to standard strength and form are essential.

In any case, even when the Lithol red dye is boiled up to give a finely divided bronzy form, there is no necessity to filter if it be required for conversion into a lake After " boiling up," the base may be stirred in and the mixture washed once by decantation, before adding the barium chloride

As a basis of comparison for a true type of pure Lithol red R, the following laboratory method is useful —

Tobias acid (commercial quality)	400 grammes (100%)
are dissolved in—	
Water (80° C)	1,100 c c
Caustic soda (100%)	80 grammes (approx)

Sufficient caustic soda is used to make the hot solution just alkaline to glazed litmus paper. This is filtered rapidly on a steam-heated filter at between 70° and 80° C leaving a muddy, brown coloured residue The hot filtrate is transferred to a beaker standing in a hot water jacket of not less than 1 gallon volume, to ensure very slow cooling The solution is slowly stirred with a mechanical stirrer When cooled to 20° C , the pure crystals of β naphthylamine-1-sulphonic acid formed will be in fairly large and more or less " detached " form. These are rapidly filtered on a vacuum filter and will be of high purity Laboratory samples of dye made from this will yield very pale and brilliant lakes of full bluish undertone

This Lithol red process has been described very fully and minute details mentioned, because it has been well tried out and found to be reliable It is also quite a typical process, applicable in its general scheme and its precautionary methods to all the reds and scarlets of this class of insoluble or semi-insoluble dyes, made from insoluble diazo compounds. The following cases requiring special modifications may be noted

(1) *Lake Red C* Modifications of temperature of coupling and balance of acidity and alkalinity in the coupling.

(ii.) *Helio Red R L* Modifications of temperature of coupling, concentration, and balance of acidity and alkalinity.

(iii.) *Lake Red P* Similar alterations to (ii.), but a different method is used, on account of greater instability of the diazo-compound

Lake red C. can be made in the same plant as Lithol red, provided a lead-lined coupling vat is used to facilitate cleaning, and the diazo vat is thoroughly cleaned out and soaked in clean water after each respective operation.

"C acid" (2-chloro-5-aminotoluene-4-sulphonic acid) is sold commercially in two forms —(*a*) as a faintly acid white paste with a slight brownish-pink cast This is the free acid. (*b*) as pale yellowish-fawn almost transparent needle-shaped crystals This is the normal ammonium salt containing ½ molecule of water of crystallisation. To avoid any errors both types when used should be calculated as free sulphonic acid.

In the following working details, it is assumed that the crystalline ammonium compound is used, as by careful crystallisation it can be produced chemically pure, because the by-products are far more soluble These are mainly :—

(*a*) Those produced by the elimination of a chlorine atom in the nitration process, and which are more soluble in the first acid precipitation of the intermediate in its manufacture

(*b*) Isomerides of "C," acid containing the same groups, but in different arrangement in the toluene nucleus

Dye Coupling Process. Start with 100 gallons of water at 25° C in the clean diazo vat, add ½ lb. .880 ammonia to precipitate any calcium or magnesium salt, and leave a slight excess of ammonia. Stir in the "C acid" ammonium salt, equivalent to 111 lbs. 100% free sulphonic acid When all the crystals are quite dissolved, add water and ice (if necessary) to give a bulk of 180 gallons at a temperature of 18° C. Stir well and precipitate quickly by the rapid addition of approximately 140 lbs 28° Tw. hydrochloric acid (iron free) ; a slightly greater excess of acid is allowed for this diazo compound than for Tobias acid *Stir for only two or three minutes* before proceeding with the diazotisation. This is done in exactly the same way as in the case of Tobias acid, using the same approximate quantity of sodium nitrite, i e , 35 5 lbs. 100% sodium nitrite dissolved in 70 lbs. of water.

The diazo compound is finished off in the same way as for

Tobias acid—carefully testing the acidity to Benzopurpurine 4B papers from time to time and continuing the addition of nitrite until a test on fresh starch iodide shows free nitrous acid after 5 minutes stirring The process should be finished at about 19° C and a bulk of 180 to 190 gallons. If pure and well made, the diazo compound is almost white, with a faint pink tinge. If it is unduly brown or fawn in colour this will be due to lack of acid in the final stage of diazotisation or to an impure grade of "C acid" (To counteract the effect of local concentration of sodium nitrite during the first rapid addition of the ¾ part, fast and efficient stirring must be maintained) The diazo compound will require careful filtration, as it is in a very fine light form. It should be filtered and treated for the coupling in exactly the same way as the Tobias acid diazo compound, with one exception, the only modification being the addition of acetic acid, equivalent to 2 lbs. of 100%, to the diazo mixture, and stirring this in for ½ hour before dropping the diazo mixture into the coupling vat. The reason for this addition is threefold —

(1) To help the subdivision of the particles.

(2) To avoid any too great local alkalinity as the mixture is dropped into the beta-naphthol solution

(3) To arrive after the coupling at a final end point, which is neutral or, even better, very slightly on the acid side.

The beta-naphthol solution is prepared as follows —

Beta-naphthol ..		72 lbs
	dissolved in—	
Water .	.	100 gallons
Caustic soda (100%)	.	19¼ lbs

and made up to 400 gallons bulk in the coupling vat Further additions of caustic soda are cautiously made until the solution just shows a faint reaction to Titan yellow paper This very slight excess of caustic soda is removed by adding 1 lb 80 per cent acetic acid in 5 gallons of water

The coupling is effected by running the whole of the diazo compound down into the beta-naphthol solution with rapid stirring, both solutions being at 22° C. The coupling may finish at 25° C without any detriment under these particular conditions, and takes place fairly quickly and smoothly Stir for at least 5 minutes after the diazo mixture is all in, then test for neutrality to glazed litmus paper, or very slight acidit when coupling is quite complete At the same time make test with 5 per cent acetic acid in a test tube as for Lithol re and a corresponding test by shaking with 5 per cent ammoni Test these respectively for free diazo compound and free bet naphthol, and continue to test until one or the other componen has been all absorbed. If the final end point is delayed for an reason, a 5 per cent ammonia solution must be run into th batch until the whole is just past the neutral point and is ju alkaline to glazed litmus If the whole of the beta-naphth disappears and leaves a small excess of free diazo compoun the latter can then be taken up by very small additions of extr beta-naphtholate (as a 1 per cent of the sodium salt solutio until a faint permanent excess of β-naphthol remains T couple this dye sometimes 3 or 4 hours' stirring are required, bu *in the latter stages* is greatly facilitated by the addition of wea ammonia until the batch is just alkaline to litmus The actua balance of beta-naphthol and diazo compound can always b determined in small tests within the first 15 minutes after mixing the components. It is of course obvious that with suc rapid addition of the diazo compound as is here described, th stirring arrangements must be of the best, giving reliabl positive agitation and intensive mixing up of the vat content

The best test reagent for the diazo compound in the rim o filter paper is an alkaline solution of H. acid, using 3 molecule of sodium carbonate to 1 of H acid. This reagent gives a ver delicate test owing to the intensity and brightness of the viole shade produced

For the detection of beta-naphthol the best reagent is diazo benzene chloride (see page 78) This couples with beta naphthol in acid or alkaline solutions, and if a spot of the reagent be dropped just outside the clear rim of the spotte out dye test, and allowed to "creep" into the edge of the rim a thin line of insoluble Sudan red forms at the junction an gradually builds up Consequently, however minute a amount of beta-naphtholate is present in the rim, a positiv result is obtained For instance ¼ lb of beta-naphthol i alkaline solution, added to a 600 gallon batch free from beta naphthol, will give a positive reaction.

Lake red C should be finished at a bulk of approximatel 550 to 600 gallons for the "½ lb.-molecule" batch describe here In " boiling up " this batch, it should first have several hours' stirring ; 2 lbs more 880 ammonia are then added in dilute solution and heating carried out slowly, up to 65° or 70° C , but certainly not higher than 70° C This gives the dye a pale brilliant orange appearance and an ideal particle form for lake making. If time permits, it is then cooled down to 45° C and salted into a filterable form by slowly sprinkling in 1 cwt of fine clean sodium chloride (dairy salt), stirring meantime The batch is filtered at 30° to 35° C in a wooden filter press by gravitation and subsequent blowing to form fairly hard cakes The average strength should be about 28 per cent dry content and the cakes are transferred to a vat to be " pasted out " with water This batch of press cake is well mixed with not more than 3 or 4 gallons of water until it forms a smooth thick paste quite free from lumps and nodules Water is then gradually added until a strength of 20 per cent is reached, then 5 lbs of 20 per cent acetic acid and 2 lbs of 50 per cent Turkey red oil are run in The slow stirring of this paste is continued for at least 1 hour. The result is a product of a pale brilliant appearance, which gives pure barium salts, pale and bright both in top tone and undertone, drying out in the ovens to an extremely soft product They are, therefore, specially suitable for printing ink lakes The presence of any excess alkali, or of a much greater quantity of Turkey red oil, than prescribed in the above formula will lead to the production of pure barium lakes, deeper in shade and drying much harder in the oven Excess Turkey red oil in particular gives a hard brittle lake on drying

LAKE RED P

Ordinary coupling methods are not satisfactory with this colour owing to peculiarities of the diazo compound. The intermediate is *p*-nitroaniline-*o*-sulphonic acid, sold commercially in a remarkably pure form as yellow crystals of the ammonium salt. This is very sparingly soluble in water, but the hydrochloride is fairly soluble in warm water containing excess of hydrochloric acid , too great an excess reduces its solubility. If the diazo compound be formed in too concentrated a solution, it at once crystallises out in very hard crystalline plates. and any such formation makes the production of a pure bright colour almost impossible At the strength given in the formula set out below, the temperature and bulk of the diazo mixture are so arranged that the major part of the diazo compound is in solution, while the very small proportion crystallises out in a very fine form

The difficulty, however, is that the diazo compound is decomposed by strong local concentrations of normal sodium beta-naphtholate or even, the weakest solutions of sodium carbonate. Therefore, running the diazo mixture into the full bulk of sodium beta-naphtholate. even if it be quite free from carbonate or caustic alkali and however quickly the addition is made, will result in a certain proportion of diazo-compound being decomposed by the alkalinity of the large temporary excess of sodium beta-naphtholate.

To reverse the process and run the beta-naphthol solution into the diazo mixture is also unsatisfactory, as the coupling does not proceed at all quickly and much of the naphthol is precipitated in too insoluble a form The optimum conditions for rapid coupling, resulting in a pure bright colour, occur at the point of change over of the mixture from *acid to neutral* The following working method based on these facts, if carried out with care, in batches of the size mentioned gives a very bright pure-toned Lake red P

Speed and accuracy of manipulation are essential to success, all reagents and materials must consequently be in readiness before beginning operations The process is carried out as follows.

Diazo Mixture ·—Ammonium salt, equivalent to 55 lbs of 100 per cent free acid of *p*-nitroaniline-*o*-sulphonic acid (mol wt 218) is stirred into 50 gallons of water at 70° C in a glazed earthenware or enamelled tank on a third floor or staging and 76 lbs of 28° Tw hydrochloric acid added This mixture is stirred until no further trace of undissolved ammonium salt can be detected with a dipping tube. The solution is then run into a sound oak vat on the stage below, containing 200 gallons of water which has been cooled with ice to 8° C. This mixing is made with good stirring and gives approximately 260 gallons of clear yellow solution at 18° C. The sodium nitrite exactly calculated by test (17¾ lbs of 100 per cent), in 30 lbs of water, is dropped into the diazotising vat, all at once

The liquid immediately turns a darker yellow, but as the reaction finishes (about 30 seconds) the diazo mixture becomes paler than the original intermediate solution. A quick test is taken and as soon as acidity to Benzopurpurine 4B and excess nitrous acid are verified, the practically clear diazo mixture is run through two 3 in. pipes into the beta-naphthol mixture contained in a lead-lined vat placed conveniently below The stirring in this coupling vat must be as fast as possible throughout, and ample space left for the heavy frothing which occurs at the end of the operation

The beta-naphthol solution which is prepared only just in advance of the diazotisation is made as follows —

36½ lbs beta-naphthol are dissolved in 100 gallons of water at 30° C with 21 lbs 100 per cent caustic soda (free alkali just to show on Titan yellow paper) This solution is run into the lead-lined coupling vat in which 150 gallons of ice water at 0° C. has been got ready, stirring well during the addition Continue to stir and slowly dust in ½ cwt of finely powdered sodium bicarbonate, and then run in 2 per cent acetic acid until the whole mixture (containing a large quantity of finely precipitated beta-naphthol) is acid to glazed litmus paper The temperature of this mixture should now be about 2° C , but if higher, broken ice must be added At this stage the naphthol mixture is ready As soon as the diazo-solution is ready it is run with vigorous stirring into the coupling vat in which the naphthol is being vigorously stirred If the naphthol mixture be allowed to stand too long, the particles form aggregates and coupling does not proceed normally The mixture should be stirred for 5 minutes and if the process has been properly carried out will be of a pale, clean, yellowish-orange shade. After the 5 minutes' stirring, a solution of 5 per cent sodium carbonate is slowly run in, until a permanent alkalinity to litmus is obtained The quantity of sodium carbonate solution will be about 50 gallons, but more should be available. Towards the end of the reaction, re-tests of the alkalinity must be made every 5 minutes as the reaction proceeds more slowly, and the alkalinity disappears after a few minutes' stirring A final stage of permanent alkalinity is reached after about 1 hour. The stirring is continued for several hours more, and then the batch is salted with 1 cwt of salt and filtered

It is not recommended to make this colour in larger batches or in greater concentrations unless very special mechanical arrangements could be provided to ensure instantaneous mixing and very fast stirring With practice in the laboratory on one-twentieth gramme-molecule batches, and subsequent practice in the works on small batches, with full attention to the mechanical difficulties Lake red P can be made of a pure clean shade, superior to the average commercial quality.

HELIO FAST RED R L.

The difficulties encountered in making this dye, true to type and uniform in quality, are due to two factors. The first is that the amino compound used (meta-nitro-para-toluidine), is very insoluble and does not diazotise at all readily unless the intermediate be in a very fine state of subdivision The best safeguard is to buy the intermediate from a maker who can guarantee to supply the paste in satisfactory form. On long storage, the fine particles form much larger aggregates, which are difficult to break up and do not react readily. The only satisfactory way to treat either a paste that has become too "granular," or the dry intermediate, is to dissolve it in sulphuric acid so that the final strength of the acid is about 70 per cent, and then very slowly pour this syrupy warm liquid into a large vat full of well stirred water The very fine suspension so formed is well washed by decantation and used at once

It should be noted that nitroamino compounds in general are very susceptible to deterioration if heated up in solution in wooden vessels, owing to the effect of the nitro group on the wood Solutions of *p*-nitroaniline-*o*-sulphonic acid and meta-nitro-para-toluidine should be handled as far as possible in stoneware or enamelled vessels if with hydrochloric acid, or in lead-lined vessels if in sulphuric acid.

Another difficulty is that the dyestuff itself is very insoluble in water, has an almost waxy nature and always forms a stodgy mass Consequently the batch is difficult to mix efficiently as the dye begins to form It is a dye which must be made in as weak solutions as possible, and in vats furnished with rapid stirring and very effective beaters

The trouble with the insoluble, jelly-like product obtained in the dye coupling is that beta-naphthol, precipitated from the solution, and traces of diazo solution become firmly embedded in the waxy particles of dye They are thus isolated and do not react. They can usually be detected by the two tests mentioned on pages 150 and 156. The only remedy is faster, heavier stirring. Any attempt to make this colour in a much more concentrated form than that given, will result in the presence of uncombined diazo compound, which will subsequently decompose. This decomposition can easily be recognised by filtering some of the batch on an open filter and cutting a piece of the soft paste dye out of the filter with a bone palette knife After half an hour's exposure, the cut surface will show brownish spots or streaks and the dye paste on well shaking with weak warm ammonia usually shows an excess of beta-naphthol

The working method recommended for moderate sized batches of this colour is as follows —

In a 450 gallon vat free from iron or brass fittings, stir 30 lbs. 100 per cent *m*-nitro-*p*-toluidine in 50 gallons of water for 15 minutes, with a cover on the vat, and well beat up the contents to break down any soft aggregates. The inclusion of 1 lb of ammonium acetate at this stage is a great assistance. Then make up to 300 gallons bulk with ice and water, at a temperature of 5° C. Add 70 lbs 28° Tw hydrochloric acid (iron free) and allow the temperature to rise to 6° or 7° C Run in the whole of the sodium nitrite in one quick operation (carefully checking beforehand the exact quantities of amino compound and sodium nitrite by titration) The amount of sodium nitrite required should be exactly 14 lb of 100 per cent The temperature is maintained at about 6° C As soon as the sodium nitrite is added stir in 1 lb of zinc oxide to accelerate the diazotisation Stir until the whole of the orange coloured suspension has dissolved to a clear solution. As long as orange coloured particles remain, stirring should be continued If carried out under favourable conditions with a suitably fine product, this will not require more than ½ to 1 hour Stirring may, however, be safely continued for 1½ to 2 hours if necessary A slightly cloudy pale yellow liquid is obtained with some brownish to greenish coloured scum and flocculent suspended matter This diazo solution must be filtered quite clear before use, otherwise bleeding in oil and dulling of the shade will result in the final colour. The solution will still show free nitrous acid fairly strongly If filtered on a wooden vacuum filter with woollen cloths, this small excess of nitrous acid almost entirely disappears, otherwise it must be removed by the addition of sufficient urea

When the whole of this clear diazo solution has been collected, it must be very cautiously *neutralised* until quite neutral to glazed litmus paper. This is best done by returning it to the diazo vat, cooling with ice to 4° C and while stirring, slowly sifting in finely powdered sodium bicarbonate, through a fine sieve There is no danger of spoiling the diazo solution if this is done carefully, even with much bigger batches. When neutral, the solution is run at moderate speed into the weak beta-naphthol solution in the coupling vat, with intensive stirring. The beta-naphthol solution is made as follows in a 1,000 or 1,200 gallon vat :—

Beta-naphthol	29 lbs	
Caustic soda .	8 ,,	(100%)

made up to a minimum of 550 gallons with water and ice (temperature 5° C). This is made just neutral to brilliant yellow paper with 2 per cent acetic acid if necessary, and then 2 lbs of sodium bicarbonate are stirred in.

When nine-tenths of the diazo solution has been added, stir for 10 minutes and verify that the mixture contains free beta-naphthol and is distinctly alkaline to glazed litmus papers.

As soon as the diazo compound is all combined, add very slowly the remaining one-tenth with constant testing The final end points are, (1) a slight excess of free naphthol by the test given on page 156 , (2) freedom from diazo compound by the test on page 150 ; (3) the dye mixture distinctly alkaline to glazed litmus paper. Stir for ½ hour, then add 2 lbs of soda ash in solution and finally, if the dye be in too gelatinous a form, very cautiously convert it into a slightly flocculent form by slowly running in about 5 gallons of 5 per cent sodium chloride solution. This will facilitate filtering without spoiling the product Turkey red oil should not be used for this dyestuff at any stage.

" Para Reds "

The original pigment dye " Para red " was simply diazotised para-nitroaniline coupled with beta-naphthol This yielded a fiery red, insoluble dyestuff with orange red undertone. It was employed as a pigment, after mixing with a suitable base, and then drying and grinding The pigment was often sold under the name of " Fire Red " Owing to its exceptional fastness to light and its great strength, together with its low cost, it was a useful bright fast scarlet for water paints and for wall paper pigments This simple type of Para red, however, bleeds excessively in oil and turpentine, and is, therefore, of no real value as an oil-paint pigment Its use in water paints and wall-papers is also to be deprecated, in view of the fact that any subsequent painting, or distempering with oil-bound water paint, will inevitably give trouble due to bleeding of the Para red into the material applied over it In fact the safe method when painting has to be done on walls papered with wall-paper coloured with Para red, is to remove the paper, or if that is not possible, to " isolate " the red by means of a good impervious coat of pure shellac knotting When Para red is present in old water paint on a wall surface, it is again best to remove the old material In the case of old red enamel or paint in which Para red is known to be present, if it is desired to repaint in a different colour, there is always a risk of bad " striking through " of the Para red, unless the old paint be first removed. These comments on the undesirable bleeding tendencies of simple Para reds have been included at this stage, because much trouble may be avoided if the pigment maker appreciates the necessity for keeping the consumer fully acquainted with this defect

The simplest Para red, as made to-day is a combination of para-nitroaniline and beta-naphthol R. (see page 164) This colour is distinctly brighter and bluer than the combination with beta-naphthol, it is also far less soluble in oil If it be made, paying special attention to the precautions given in the formula on pages 164 and 165, there is very little tendency to bleed in oil Careful preparation and manipulation of the diazo solution is important, as any decomposed diazo-compound causes excessive bleeding

Other closely related dyes are Autol reds, Toluidine reds, etc. The compounds of nitrotoluidines with beta-naphthol, although really homologues of " Para reds," are not classified with them and do not bleed so readily in oil when correctly made.

A vivid fast scarlet pigment of this type is used in dyeing and calico printing It is made from diazotised para-nitroaniline and Naphthol A S (anilide of 2 . 3 beta-oxy-naphthoic acid) This colour is also used as a pigment In dyeing and calico printing numerous pigments of this type are widely used under the general term of " ice colours," the name being derived from the fact that large quantities of ice are used to keep the diazo solutions cold.

A works process for Para red is as follows :—Dissolve 70 lbs of good quality dry para-nitroaniline in —

Boiling water	35 gallons
Hydrochloric acid (28° Tw)	260 lbs

This should be done in a large glazed earthenware vessel. When dissolved, pour the hot solution into the diazo vat in which is stirred a mixture of 6 cwts of broken ice and 200 gallons of water. Most of the para-nitroaniline hydrochloride will be precipitated as a fine suspension, which is essential to success The temperature must be lowered to at least 5° C. using more ice if necessary, then stirring vigorously, add the sodium nitrite solution in one lot, as rapidly as possible

Nitrite Solution.

Water	8 gallons
Sodium nitrite (98%)	35½ lbs

The diazotisation is quite rapid and when completed a very pale yellow, almost colourless solution, free from suspended matter or tar, is obtained. If there be any cloudiness or tarry matter, it is advisable to filter through a fine woollen cloth at this stage This clear solution is maintained at 6° or 7° C. and run fairly slowly (during about 15 minutes) into the naphthol R solution.

Naphthol R	76 lbs
Caustic soda (98%)	40 ,,
Soda ash .	40 ,,
Turkey red oil (50%)	30 ,,
Water . .	350 gallons

Made up to a clear solution and cooled to 15° C.

The 76 lbs. naphthol R can be made up in the solution from its two components as follows —

β-naphthol ..	65 lbs.
Casella acid (β-naphthol-7-monosulphonic acid	11 ,,

The essential points are —

1 To keep to the relatively large excess of acid shown in the diazo solution (and corresponding excess of alkali in the naphthol solution)

2 To add the nitrite to the para-nitroaniline as an almost instantaneous operation.

3. To add the first half of the diazo solution to the naphthol solution fairly quickly and the remainder slowly, with good stirring

4 The final end point to be distinctly alkaline

If a reduced strength of Para red be required, it is advantageous to suspend the necessary base in the naphthol solution before coupling This gives a more intimate mixture with less tendency to bleed

Pigment Scarlet 3B (Or the equivalent I C I product, Pigment Carmine 3B) This is a soluble dyestuff, which very few lake colour manufacturers would find profitable to make in their own plant, as it can be bought cheaply in bright standard quality There is no very great difficulty in the actual coupling operation and the diazo compound is far more stable than is generally supposed For instance, in the laboratory formula given here, the acid diazo solution is neutralised with 10 per cent sodium carbonate solution This method can be safely employed for works batches of a half-pound-molecule.

As the working method is the same for a works process, and as the preparation of a small laboratory batch of the dye forms the best method of judging the purity of both of the components (R. salt and anthranilic acid), a carefully tested and proved laboratory method is given below—

Diazo Anthranilic Acid 6·9 grammes 100 per cent anthranilic acid are dissolved in 150 c c. hot water, with 12 c c. of 28° Tw. hydrochloric acid. Ice is added and the temperature lowered to 3° C , then 3 5 grammes of 100 per cent sodium nitrite in 10 c c. water are added in one operation, with good stirring The solution should be very pale yellow, and must show a definite reaction for free nitrous acid It will usually contain traces of flocculent particles of impurities and possibly traces of tarry scum It is filtered at this stage, and after standing 10 minutes is made neutral to glazed litmus paper, by adding 10 per cent sodium carbonate (about 35 c c) The temperature should be kept below 5° C and the solution be pure yellow in colour, with no tendency to red or brown This solution (300 c c bulk) is run at moderate speed into a well stirred solution of *pure* R salt (β-naphthol-3—6 . disulphonic acid free from all isomeric acids), prepared as follows —

R salt	.	18 0 grammes (100% on basis of mol wt 248)
Soda ash		16 0 „
Caustic soda		1 0 „ (100%)

in 500 c c bulk of water at 12° C

The addition is made more slowly towards the end and coupling proceeds smoothly A distinct excess of R salt must be present at the end.

At this bulk of 800 c c and a final coupling temperature of 12° to 14° C , the reaction mixture will show only a *very faint* clean pink colour in the filtrate from the dye, *without the addition of salt to precipitate the dyestuff* Should the filtrate at 15° C be at all strongly coloured, especially if it be possible to " salt out " from it, a full red dyestuff, the presence of monosulphonic acid (Schæffer acid) and isomeric disulphonic acids (6 8 and 3 . 7) may generally be assumed

If the pure dyestuff, filtered off at about 16° C (without any addition of salt) be made up into lake on a suitable substratum, the lake has a dull bluish undertone and low tinting power If, however, very small percentages of both sodium carbonate and sodium sulphate are added to the dye solution before adding the precipitant, a lake of much paler, brighter top tone is obtained with a bright rosy undertone and greater tinctorial strength This is due to the much superior dispersion of the dye over the substratum, effected by the combined action of the extra alkalinity, and the simultaneous precipitation of barium carbonate and barium sulphate, which takes place on adding the barium chloride Deeper shades, which are not so bright, are obtained by omitting the sodium sulphate in the dyestuff.

In the commercial dry dye powder, it will be found that very small additions of these necessary ingredients have already been made Up to a certain point a still lighter, brighter shade can be obtained if the lake be made in more dilute solution with a small extra addition of sodium sulphate.

To prepare a sample of pure R salt, irrespective of yield, for use in the preparation of a standard sample of Pigment scarlet 3B , proceed as below

Dissolve 100 grammes of commercial R. salt (calculated as

100 per cent molecular weight 348) in 600 c c. water at 75° C. Run in 26 grammes of pure fresh calcium hydroxide suspended in 50 c c. of hot water Stir at 70° C for 10 minutes. Filter on a vacuum filter and wash the precipitated calcium sulphate with 50 c.c. of boiling water The hot clear filtrate, about 700 c c in bulk, is converted into calcium salts by adding 28 grammes of calcium hydroxide (100 per cent) in 25 c.c. of water. This mixture is allowed to cool slowly to 14° C, then the crystalline precipitate is filtered as free from mother liquor as possible. This filter cake is dissolved in 400 c.c. of boiling water and 50 per cent sulphuric acid added until the mixture is just acid to Benzopurpurine 4B. The calcium sulphate is filtered off and the strong filtrate obtained is " salted " at 75° C with 125 grammes of salt, well covered up and allowed to cool very slowly. The distinctly crystalline precipitate of R salt (acid sodium salt of mol wt 326) is filtered to a hard cake on the vacuum filter. This method gives just over half of the original R salt in a remarkably pure form The remainder is in the various filtrates and calcium sulphate filter cakes, along with all the isomerides

Small laboratory batches of the commoner dyestuffs, such as Ponceaux, made from this specially purified R. salt, show a remarkable difference from the commercial product, particularly in blueness of undertone and in greater insolubility of the barium lakes in comparison with the ordinary commercial dyes. This purification process, however, is wasteful, but is of great use for obtaining a laboratory standard as a basis of comparison and test

Naphthol Green B. As in the case of Pigment scarlet 3B, it seldom pays the lake maker to produce this dye. A laboratory method is given below, as a matter of interest to the chemist, who requires a standard sample The main difficulty in producing this on a works scale is that the nitroso compound sets very stiff, therefore adequate stirring is necessary to avoid the deleterious local action of nitrous acid, at the point of addition of the hydrochloric acid, and such stirring is not easily maintained Any further dilution of the batch to avoid this, causes loss of dyestuff because of its great solubility

Laboratory Method. 95 grammes of 100 per cent Schæffer acid (100 per cent mol wt. 223) are well beaten up in 400 c c of water until free from lumps This mixture is diluted in a large glass vessel to 1,200 c c bulk with ice and water at a temperature of 5° C

15 grammes of 100 per cent sodium nitrite are then added and the stirring continued for 15 minutes The stirrer must be robust, and capable of a protracted run At this stage the acid is run in from a vessel with a small tap, one drop at a time, so that the total mixture of—

Hydrochloric acid (28° Tw)	58 c c
Water	300 ,,

requires 1½ hours to add During the addition the mixture is a bright brownish-yellow, gradually darkening and becoming more soluble Stirring is continued for half an hour, and then 2 grammes ammonium chloride added to serve as an alkali indicator later.

46 grammes of pure, powdered ferrous sulphate, and 7 c c. of water are slowly added and the stirring continued for 15 minutes.

Finally, 10 per cent caustic soda is slowly run in until a faint odour of free ammonia persists (about 250 c.c. are required) The dye is all in solution at this stage, but after standing several days about 30 grammes will generally crystallise out The complete dye solution as prepared may be used directly by adding the bases and precipitating.

If a mixture of Cassella (β-naphthol-7-sulphonic acid) and Schæffer (β-naphthol-6-sulphonic acid) acids be used a brighter bluer, Naphthol green is obtained which has slightly less solubility in water. The laboratory process given, results in a small wastage of Schæffer acid, but ensures that no loss of dye or dulling of shade occurs through excess iron and the consequent formation of ferrous hydrate, which in its turn acts as a precipitant for some of the dye

Ponceau Reds Ponceau Reds were among the first reds to be made by pigment colour manufacturers, but to-day owing to the much superior strength and fastness of pigment dyestuffs, such as Lithol red, Lake red C., Permanent reds, etc , their use has become distinctly limited. Very few pigment colour works continue the manufacture of these dyes, because the small quantities used are best prepared from standard ready-made dyes bought in powder form It therefore seems unnecessary to give any working formulæ The main essentials for their manufacture are quick accurate diazotisation of the aniline or xylidine respectively in weak solutions only (1 to 2 per cent), and the use of at least 2½ equivalents of acid to 1 of amino compound to avoid the formation of diazoamino compounds. The solutions must be kept cold (below 3° C in the case of xylidine) and excess diazo solution carefully avoided Impure intermediates generally give dyes, which yield lakes of poor brilliance and not sufficiently insoluble in water after they are struck This last statement really only applies to Ponceau R. from xylidine and R salt

Pure Ponceau 2R Pure Ponceau 2R gives a very insoluble lake with barium chloride, with a very bright and blue undertone, and is prepared by using pure meta-xylidine and a specially purified R salt. This is much superior to the ordinary Ponceau R., in all respects, and is well worth making if the correct intermediates can be obtained cheaply.

The manufacture of these dyes from intermediates is only profitable when there is a sufficiently large and consistent demand for lakes made from them

It does not pay for the really small colour manufacturer to enter into the manufacture of a number of these dyes for his own use, although he may quite well specialise on any one which his plant is capable of handling on a big enough scale. On the other hand, it is not reasonable to expect the large dye making concerns, with their highly organised works and skilled workers, and attendant responsibilities and expenses, to forego some of the proper return for their skill and enterprise, by supplying pure intermediates too indiscriminately.

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CHAPTER XIII

PIGMENTS PRODUCED BY DRY BLENDING IN THE EDGE RUNNER MILL

THE reduced Brunswick or Chrome greens made from dry blue and dry yellow, with the required base have been described on page 137 In making this series, it is often an advantage to give the yellow and the base a short preliminary grinding before adding the blue. In finishing the greatly reduced qualities, a small percentage of machine oil is used by some makers to give a rich tone to the dry powder and counteract the rather chalky appearance which is produced by the use of a large proportion of base or " extender " Machine oil should never be added, even in small quantities, because as a result of its greasy nature it spoils the quality of the paint in which it is used, and its effect is merely to give a spurious, rich appearance to the dry powder A good appearance can always be assured by finally grinding in a " Kek " mill, after the pan mill " blending " and " developing " This final grinding in a " Kek " mill is known as " dressing " and is a most important part of the treatment of all colours made on the edge-runner. Very few trades to-day can afford to buy or use dry colour which is harsh or gritty, and the passage through the " Kek " mill ensures a good saleable product

The special range of organic pigment dyes which can be used to produce good lake or pigment colours, rapidly and at a low operating cost by grinding or rather " developing " with the dry base in an edge-runner mill, includes many colours of several different chemical types

All the pigment dyes used for this purpose have two properties in common—

1 They are insoluble or practically insoluble in water

2 They yield uniform, well dispersed lakes or pigments by dry grinding with the base or substratum, and neither need, nor combine with, a precipitating agent.

There is also a sub-class comprising a few special acid-azo and mordant dyestuffs, which although normally soluble in water are sold by the dye makers as ready prepared insoluble metal salts of the dyes These are usually exceptional cases, in which secret or special methods of obtaining the correct " dispersion " and brightness of the dye lakes in question, are used by the dye producers. Two notable cases are

(*a*) Helio Red R M.T. the best and brightest shades of which are sold as an insoluble powder of the lead salt of the dye. The dye itself may also be purchased, and precipitated on to a suitable base, as lead or barium lake

The dye is diazotised meta-toluidine sulphonic acid ($CH_3 = 1$; $NH_2 = 3$, $SO_3H = 4$) coupled with beta-naphthol

(*b*) Helio Bordeaux B L , paste, which according to some authorities is produced from " R. " salt, and according to others is a compound of alpha-naphthol (4 or 6) sulphonic acid, is probably a combination of diazotised *p*-toluidine-meta-sulphonic acid and alpha-naphthol-5-sulphonic acid.

It is sold as an insoluble paste dye or as a dry powder in the form of the calcium salt, which is in a remarkably fine state of sub-division and quite insoluble in water. The free dyestuff, which is not marketed, is quite soluble in water The soluble dyestuff, if converted into lakes by ordinary methods, yields heavy, more or less crystalline lakes of poor appearance and colour This is probably the reason why special methods have been evolved by the dye-makers to enable them to offer finely-divided metallic salts of these two dyes in a form suitable for simple edge-runner mill development Helio Bordeaux 2B is reputed to be the barium salt of the same dyestuff as is used for Helio Bordeaux B L

The members of the main group of dyestuffs, in which the free dyestuff itself is insoluble, all possess characteristics which are important from the point of view of lake-making, namely, ease of sub-division and efficient adsorption on the base or substratum, and little or no tendency to bleed in oil

These characteristics are imparted by the presence of at least one *weak* acidic group in the toluidine residue of the amino compound The best of the series (mostly yellows, oranges and scarlets) contain one or two nitro groups or chlorine atoms and in some cases one chlorine atom and one nitro group.

A discussion of the most favourable positions of these various groups in the molecule, in relation to general lake-making properties, and more especially fastness to light, is given by R. Stæble.

Many of the totally insoluble pigment dyes and a few insoluble pure metallic salts of dyes, for example Helio Bordeaux B.L. calcium salt ; Helio red R M.T lead salt , Lake red C. barium salt, are put on the market by dye makers in the form of dry powders, which are particularly adapted for the cheap and rapid manufacture of pigment colours by the simple process of grinding or "developing" the dry dyestuff with a suitable dry base in an edge-runner mill This operation can be economically carried out on almost any scale, small or large, and the expense of preparing and cleaning up plant is almost negligible compared with that in a wet colour process. The types of pigments which can be successfully produced in this simple way are mainly included in the following list, with the addition of the three special metallic salts mentioned above :—

LIST OF INSOLUBLE POWDER DYES FOR PAN MILL DEVELOPMENT

Yellows in order of shade from greenish-yellow to orange

Made by J W Leitch & Co

Citron	Pigment	Fast	Yellow	H	10 G L	Extra
Primrose	,,	,,	,,		5 G L.	,,
	,,	,,	,,	G	R L	,,
	,,	,,	,,	H	6 G.L	,,
Lemon to Transparent		,,	,,		T B	,,
Middle	Pigment	,,	,,	H	G L	New
	,,	,,	,,		R L	Extra
	,,	,,	,,		2 R L	,,
Pure Orange	,,	,,	Orange		5 G L	.
	,,	,,	,,		H F L.	.
Orange Red	,,	,,	,,		L	,,

Many of the foregoing are pyrazolone colours, whilst several are acetoacetic azo derivatives of anilides and toluidides

Parallel types and shades are manufactured by British Dyestuffs Corpn , Ltd , and by Continental firms, ranging from greenish-yellow to orange

Scarlet to red shades *British Dyestuffs Corpn., Ltd.*

(B.D.) Monolite Red 2 G.
(Diazotised 2 : 4-dinitraniline coupled with beta-naphthol, which being highly nitrated must never be dry ground with any lead compounds.)

(B D.) Monolite Fast Scarlet R N Lumps
M-nitro-*p*-toluidine and beta-naphthol.

(B D.) Monolite Red R Powder.
Tobias acid and beta-naphthol.

(B D.) Monolite Red B Powder
Ranging from orange-scarlet to full red shade.

Pigment fast reds and greens manufactured by J. W. Leitch & Co., are as under:—

Pigment Fast Red	P R L	Extra New
,, ,, Scarlet	B L	,, ,,
,, ,, ,,	5 R L.	,, ,,
,, ,, ,,	B P L	,, ,,

Pigment Green B Powder (An iron *salt* of nitroso-β-naphthol.)
(B D.) (Leitch) and (I G.)
,, ,, 3B ,, (Beta-oxy-naphthoic isomer.)

More comprehensive lists of dyes suitable for lake making, made by several British manufacturers, are given in the appendix.

(M L B.) Hansa Yellow	10 G	Diazotised *p*-chloro-*o*-nitroaniline combined with acetoacetic-*o*-chloroanilide
(M L B.) ,, ,,	5 G	*o*-nitroaniline with acetoacetic-anilide.
(M L B.) ,, ,,	3 G.	*p*-chloro-*o*-nitroaniline with aceto-acetic anilide.

Hansa yellow G R (M L.B.) is a pale rich orange yellow, a very useful shade for richening and yellowing brown pigments. (Mennige Ersatz C.)

Red lead substitute (I G.) originally "Brilliantone Orange (Griesheim)" is a strong cheap pigment orange of brilliant orange lead oxide shade. It is of good fastness to light and lime, but tends to bleed in turpentine and solvents.

(A G F A.) Permanent Yellow R	Diazotised *o*-chloroaniline coupled with 1-*p*-nitro-phenyl-3-methyl 5-pyrazolone.
(A G F A.) ,, ,, 4 R	The same without the nitro-group

These are typical pyrazolone colours of middle yellow shade, The two greens mentioned on page 173 are very fast to light and to lime, and are the only representatives of this type of colour in general use.

BLUE "PIGMENT" DYES

One of the best is a combined shade made by precipitating Methylene blue (basic dye) with a bright Acid alizarine blue. It is sold by the I G as an insoluble powder ready for pan mill development under the name Helio Marine 2G L (D R.P. 301,555)

It is of excellent fastness to lime, light and water and is rather brighter than corresponding shades of reduced Chinese blue Being very strong in staining power, it forms an excellent pigment for cellulose lacquers

All of these insoluble pigment dyes generally sold in dry powder or in soft lumps, can also be obtained in paste form, and generally a slightly brighter, stronger pigment is obtained from the equivalent amount of the paste dye, owing to the high degree of dispersion of the particles. This applies especially to Helio Red R.L and, therefore, when it is necessary to ensure the maximum brilliance with a given type, the paste form should be used. This entails an additional stage in the process of manufacture, but not a costly one, viz , puddling up the paste dye in a small vat or tub, with the base and just enough water to form a stirrable mass This stiff paste is dried, and the dry product ground in the edge-runner mill to develop the shade and to secure the required intimate mixture. The dry pigment dyestuffs, on the other hand, have the advantage of requiring less storage room and costing less for carriage

Although the paste dyestuffs are rather more wasteful in storage and manipulation, they undoubtedly give rather brighter and stronger pigments

Other processes for the production of pigments direct in the edge-runner mill have been described by various writers, but do not appear to be at all widely or regularly used

Two of these processes are described below—

1 Cheap grades of lime greens or similar colours can be made by spraying a concentrated solution of the chosen basic dyestuff in mixed water and alcohol, or even in hot water alone, on to dry green earth in the pan mill This spraying and grinding in is done simultaneously Assuming a 20 per cent solution of a soluble type of dye (equal parts of alcohol, and

water) and a final product with 2 per cent dye content, the total water and alcohol used is approximately 8 lbs per 100 lbs of product During the grinding, most of the alcohol and water evaporates, leaving a final product with about 2 per cent moisture The process is not satisfactory, as the distribution and dispersion of the dyestuff over the green earth particles is very inadequate, with a consequent wastage of dyestuff and dullness of shade in the product

2 The production and development of cheap Lithol red pigment by grinding together dry Lithol red dye and the base, then spraying the mixture with barium chloride solution, and grinding until the small percentage of introduced water has mostly evaporated. This of necessity involves long grinding and has two other disadvantages—

(*a*) incomplete conversion of the dye into the barium salt ,

(*b*) production of sodium chloride, which is retained in the finished pigment

The process can scarcely be termed a workable one, but is given as a matter of interest to illustrate the variety of working methods which have been tried.

Two other important series of colours are produced by careful grinding together in a pan mill, with subsequent finishing in a "Kek" mill for high class grades. These are —

1 A range of bright, fast, leadless greens made from either blue lakes or bright greenish shades of Ultramarine, with fast pigment yellows and

2 Fast reddish-violets made from reddish toned ultra blues with bright bluish-red bordeaux or crimson lakes

Very good fast colours can be made in either range, provided the ultra blue used be of first-class quality, bright and strong, with the correct undertone—i.e , for greens one with a pure blue-green undertone, and for violets, one with a rich purple or reddish-blue undertone

Mixed greens of good bright middle shades, of great fastness to light and lime, can be produced by using a pure greenish Ultramarine with Hansa yellow types (Monolite Yellow G S lumps B D C) and, if necessary, zinc oxide for paleness and opacity Still brighter, paler shades can be made by using pale greenish-yellows of the pyrazolone class, such as Light Yellow 5G L. Extra (Leitch). Two cheaper bright yellows which may be used are Pigment Chlorine G G and Lithol Fast Yellow G G , which are formaldehyde condensation products.

The last two chloro-*o*-nitroanilides have the disadvantages of slightly bleeding in water, and completely subliming below 150° C

Bright shades of greens may be produced from Methylene blue B. lake, or similar shades of dye lakes, with the same range of yellows, but they are not so fast, and are already superseded by really fast shades obtained from mixtures of "Fanal" colours

It is a difficult matter to produce fast lakes in bright reddish-violet shades, and only the richest bright shades of Ultra blue with a pure *reddish* undertone can be used The red component must also be chosen with care and should have as *bluish* an undertone as possible.

Generally speaking these shades are used for transparent lakes, and any attempt to make them really opaque only results in a muddy or flat shade A brighter, paler colour can usually be obtained by selecting a bluish-red lake with a clean pale top tone It must be borne in mind that the top tone as well as the undertone of the red lake used for making a reddish-violet shade, must be bluish in tone Pure Ponceau 2R and 3R. are good examples, but they are not very fast to light

In making mixed shades from various component dry colours or lakes, care must be taken to test the fastness of the actual mixture proposed, as such mixtures as Zinc chrome with certain types of Ultramarine, may not be by any means fast, owing to the interaction of two components (one *with "reducing" properties* and one with *"oxidising" properties*) This may be purely a chemical interaction, but still will not occur *except under the influence of actinic light*, hence the necessity for testing all such mixtures under the actual conditions in which they will be used.

An important requirement for any blue lake to be used in making combined shades by dry grinding only, is that it shall not bleed in the particular vehicle in which it is to be used For instance, red-violet shades made from blues and reds will give disastrous results in oil paints if either component bleeds in oil

SECTION 5

LAKE PIGMENTS

CHAPTER XIV

BASES

THE following chapters deal with actual colour making processes in detail. As far as possible the grouping has been chosen so that all colours made by similar working methods and in the same type of plant, are dealt with in one chapter. In other words, a classification by process, rather than a chemical classification, has been aimed at

Practically all of these colours are " struck " on a base or substratum, with the exception of pure Iron blue, the range of " Reflex " printing ink colours, and deep shades of Chrome yellow. For this reason the various " bases," their uses and special properties, have been dealt with in this preliminary chapter

A very useful brief survey of all types of bases, with several working formulæ for alumina and similar bases, is given in the Imperial Chemical Industries booklet " Colour Lakes," issued by British Dyestuffs Corporation

As the base or substratum plays such an important part in regulating such factors as the price, the oil absorption, the covering power, and even the shade and undertone of all colours, the subject is treated here in detail

Bases are used in two distinct ways in pigment manufacture

1 As ready made substrata

2. As simultaneously precipitated ingredients in the colour " striking " process

Both types of base are so often used in the same colour process and as most colours are prepared by both methods, e g , barium sulphate may be used as ready-prepared blanc fixe, or precipitated in the colour striking, etc , it is not possible to classify them further by this method. The use of at least part of the base as a " simultaneously precipitated " ingredient, in general gives better covering power and a finer, more homogeneous product It will, however, often tend to make the full shade of the pigment flatter and paler in oil and, therefore, can only be put to a limited use For example, in the case of rich shades of Chrome greens, which appear too milky and flat, if barium sulphate is precipitated in the making or if too much lead sulphate be included in the formula. Ordinary acid Ponceau reds also are too milky and flat if barium sulphate be simultaneously precipitated in them

ALUMINA BASES

Alumina bases, including mixtures of aluminium hydrate, phosphate, and arsenite, are used in practically all strong fine organic colours of the lake type where a fine soft dry-colour is required, and where transparency and richness are essential. For high grade printing inks and for deep rich shades of lake colours for artists, coach paints and all similar work, alumina either alone, or very often with a smaller proportion of phosphate, is the base In all these cases the hydrate should be made with only a slight elevation of temperature and must be washed quite free from sulphates, if it is to give lakes free from milkiness. When the subsequent precipitation involves calcium or barium salts, alumina paste containing sulphates will produce traces of barium sulphate or calcium sulphate, which will impair the transparency and richness of the lakes

The temperature, concentration and rate of precipitation, all affect the form and general qualities of the alumina so greatly that extreme care must be exercised in determining the exact quantities and procedure which give a suitable product, and then the standard working methods must be adhered to in all particulars.

A process which gives a good quality alumina is as follows —

Dissolve 1 cwt of aluminium sulphate (18 per cent Al_2O_3 content) in 130 gallons of water at 100° F. This should be done, if possible, in a very tall shaped vat of about 600 gallons capacity, to allow of easier settling and washing The stirring must be very efficient and rapid if a fine uniform product is to be obtained

With good stirring, slowly run in, over a period of approximately 10 minutes, reducing the rate towards the end, a solution of 52 lbs water-free soda ash (99 per cent) in 60 gallons of water at 100° F

Stir for $\frac{1}{4}$ hour, and if a very fine light alumina is required, wash with pure cold water and allow plenty of time for the first settling Three to four washings will be necessary, or more if the settling is bad. The alumina is finally filtered in a press.

The batch of wet cakes of alumina should be collected together in a small clean vat equipped with a stirrer and well stirred into a smooth stiff paste, then *slowly* diluted to a prearranged depth in this small vat to give an absolutely standard " slop " of say 5 per cent strength To ensure freedom from lumps, the first stirring-up of the cakes without additional water is essential, and the first additions of water should be made in half gallons at a time, so that the " thinning " of the paste is very gradual A paste of known strength (calculated from the original Al_2O_3 content, and the final gravity and bulk) is the most convenient and safe form of alumina for general use.

The above method can be quickened by the use of salt solution while stirring the precipitated alumina slowly run in (after the first 15 minutes stirring) 4 lbs. common salt dissolved in 10 gallons of water This will cause a considerable flocculation of the completely formed alumina, and the precipitate will settle down very much lower in the vat and much more rapidly. The first washing thus removes a large proportion of the soluble sulphates In the second washing, use clean water and stir 10 minutes, then again run in salt solution slowly, this time 2 lbs. only in 10 gallons water. The washing and settling will again be rapid and efficient. Wash twice with clean water and a very pure product is obtained If in the final washing the stirring is continued for some time, the alumina will have deflocculated to its original form If on the other hand a mere trace of salt is not objectionable and rapid filtering is advantageous, the 2 lb salt per washing can be continued right up to the pressing stage The alumina can be washed partly free of these traces of sodium chloride in the press and will again deflocculate on thorough stirring with water to make the standard strength " slop " The precipitation is best finished very slightly acid Free alkali in the finished base causes a characteristic hardness in the finished lakes.

The production of alumina at 80° C. and over is sometimes advocated, as a dense, easily washed precipitate is obtained—for the same reason more concentrated solutions are also used, but these methods are only to be recommended for a very dense form of alumina, such as is required for some paper-surfacing colours To make at lower temperatures or lesser concentrations than the example given, is usually too lengthy an operation and therefore impracticable on account of cost.

In filtering the paste obtained in the example given, a paste of not more than 10 per cent alumina content will be obtained, and with the salt addition continued in each washing the cake will be obtainable up to 12 per cent, with also much better " draining " or filtering quality It will thus be seen that a convenient strength to make the product for use as a smooth uniform cream will be say 5 per cent or 3⅓ per cent, so that calculations are simplified in weighing out for a batch

Caustic alkali is not used, even in part, for the precipitation of alumina for use as colour base, owing to the very gelatinous form of precipitate obtained and the objectionable hardness of the finished colour if made from this type of alumina.

ALUMINA BLANC FIXE

Alumina blanc fixe is used for cheaper, denser lakes where opacity is of importance, such as in surfacing colours for paper, fine distemper colours, water colours for artists' use, etc It is usually produced as a primary and secondary reaction, using the sodium sulphate produced in the alumina reaction, to react with the barium chloride added to the later stage.

Taking as an example the batch of alumina hydrate given on page 178, this would be made at about 160° F. and after precipitating the alumina, it would be kept stirring and a solution of 56 lbs barium chloride ($BaCl_2$ $2H_2O$) in 60 gallons water at 160° F slowly run in (taking about 5 to 6 minutes for the addition) This combined precipitate will settle more rapidly and can thus be more readily freed from the sodium chloride left in the mother liquor

ALUMINIUM ARSENITE AND PHOSPHATE

Aluminium arsenite and phosphate are used where greater brilliancy is needed The arsenite often gives very bright shades which are rather fugitive to light, and the precipitated lakes are more slimy and difficult to handle. For this reason the arsenite is seldom used

The phosphate is quite a usual constituent of bases in madder, cochineal and alizarin lakes, in fact it appears to be an essential ingredient of most bright shades of madder and alizarin lakes. Lakes containing a fair proportion of aluminium phosphate tend to have slightly less fastness to light, than those on pure alumina, but not to such a degree as is the case with " arsenite " lakes Lakes with a high percentage of arsenite or phosphate also tend to dry hard.

These two bases are generally a part constituent of a hydrate base and are not prepared separately, and are, therefore, included later as items in the corresponding colour processes.

BARYTES

Barytes is the most important base for the production of cheap pigment colours for the paint and linoleum trades It has the advantages of being obtainable in large quantities as a pure natural mineral, cheap in price, of great purity, uniformly white, and quite inert to all ordinary paint media It also possesses one other advantage which is not always mentioned, viz , that its fine hard particles greatly assist the rapid grinding and development of many of the ordinary mineral colours (chromes, greens, blues), Lithol red, and other colours which have to be produced at the lowest price in large quantities It usually pays best to buy barytes of good colour and finely ground Its valuation and purchase should be controlled by examination under the microscope for particle size and shape A high percentage of silica is a disadvantage as it greatly increases the oil absorption figure. Barytes for use in lakes of importance should be carefully tested for calcium compounds and for silica

Silica may be suspected, in moderate quantity, if the oil absorption of the barytes appears unduly high. Calcium compounds will often interfere with the actual shade of lakes or pigments struck on barytes. These two impurities can be identified by fusing a small sample of the barytes in a platinum crucible with microcosmic salt, and determining any silica as insoluble matter after dissolving in hydrochloric acid, and then separating any calcium in the soluble part

It will generally be found advantageous to include some barytes (but only of the finest grade possible) in pigments which are to be struck on blanc fixe, in order to increase the opacity and smoothness of spreading essential in paper colours, or the better suspension in oils and varnishes of pigments for paints and enamels With some barytes present, the oil absorption is not too high, and the grinding and full development of shade proceed more rapidly.

BLANC FIXE

Blanc fixe or precipitated barium sulphate, is of great importance on account of its inertness, its extreme fineness and good white colour. It is more often used in conjunction with other bases, as already described, than alone. It can, in some cases, be used alone with advantage as the base on which strong organic dyes or pigments are struck, notably for high-grade pigments, for enamel paints and cellulose enamels, in which the proportion of base to actual colouring matter is relatively low With very concentrated lakes the higher oil absorption is no great detriment.

For instance, lakes of such colours as Helio reds and yellows, Lithol red, Lake red C , Permanent reds, and Pigment green, will make excellent pigments for high-priced oil enamels if at a concentration of about 25 per cent dyestuff, and for cellulose enamels if struck on blanc fixe at a concentration of at least 40 per cent up to 60 per cent dyestuff in the pigment In these two cases the essentials are strength, fineness of particle and permanence of suspension. Great opacity is not essential, although desirable, but fair covering power is a great advantage, although these types of "finishes" are always applied over groundwork, which has been brought up to as near the shade of the finish as possible.

CHINA CLAY AND COLLOIDAL CHINA CLAYS

China clay, usually the "colloidal" varieties, such as Catalpo, Stockalite, Devolite, are used in small proportions with many other bases to give greater bulking and better suspension properties, and in larger quantities in good quality pigments for water paints or distempers, in which a light soft filling material is required for a strong dye or pigment of dark shade It has the advantages of being relatively inert, soft and light, and when used in water paints has the property of forming strong continuous films owing to its particle shape,which helps it to "knit" together in the film Its chief use is in paper surfacing colours where polishing properties are required, and some grades of catalpo acquire quite a high polish in the finished colour film, under pressure

Green earth (and white earth) are of outstanding importance, although only used for one big class of colours—lakes from basic dyestuffs. They are indispensable for this valuable and special range of colours. Green earth, and to a rather less degree, white earth, possesses the property of precipitating basic dyestuffs from their solutions The percentage weight of dyestuff which can be "precipitated" on to the base, varies both with the dyestuff in question, and even more so with the actual type and properties of the earth. A really suitable green earth is very difficult to obtain, but is of paramount importance Some green earths of very pale, light green shade will give a much dirtier dull shade of lake with a pure green dye than some other green earths, which in themselves are of a deeper dirtier shade before converting into a green dye-lake. As so much depends on the physical properties, and to a less degree on the chemical properties of colour earths, they are again referred to and a fuller account of their use given in Chapter XVI.

White earth must be used for such colours as basic reds, violets and pale yellow, where any pronounced green shade of the earth itself would dirty the shade. Sometimes a very pale, clean shade of green earth may be used quite successfully, and even if a white earth has good "precipitating" properties and be pure white, it does not follow that it will produce a lake without dulling the shade of the dye A careful test of this point must be carried out with all deliveries of both green earth and white earth. According to the Imperial Chemical Industries booklet, lakes on white earth are generally less fast to light than those from the same dyes on green earth This is an important point in making a choice.

Gypsum or Calcium Sulphate

Gypsum or calcium sulphate (often spoken of as "mineral white") is very little used in the majority of ordinary lakes and pigments for paint and paper colours. It is used to a small extent in some alizarin lakes where its presence is desirable Its principal use is for distemper colours, which are sold as "dry distempers" in the form of a powder containing dextrin, glue, or casein binders (along with soda ash in the last case) For this purpose and when used in water paints, its slight solubility in water is an advantage A minute film of calcium sulphate is deposited throughout the distemper film when the water has dried out after application, and this assists the binding together of the whole film and its better adhesion to the wall.

LEAD SULPHATE

Lead sulphate is not often produced by an independent process for use as a base, but is precipitated as an essential ingredient up to a fair proportion, in all lead Chrome yellows of primrose and lemon shades, and in all lead Chrome greens. In these cases it must be regarded as a base, as the chromate proper is dispersed over it in a fine form The shades in question owe their particular appearance to the whiteness and opacity of the lead sulphate The sulphate thus serves both as an extender and as a base for the chromate White lead (basic carbonate) although more opaque, cannot be used for this purpose, for owing to its basic character, all pale shades of Chrome yellows and Chrome greens, would be turned dark and dirty in the drying Lead sulphate is occasionally used to give a paler and more opaque pigment from dark, transparent types of pigment dyes, such as Pigment green B , when required for paint work. It is more customary to use zinc oxide or lithopone for this purpose, because although the light fastness of most organic colours is less effected by admixture with lead compounds than with zinc compounds, the majority of them are required to resist sulphuretted hydrogen, which is often present in traces in the air of large towns

OCHRES

Ochres, particularly of the very pale, silicious grades, are used as bases for the production of rich dull shades of yellows and greens, such as marigold yellows and olive greens, both for paint trade pigments and pulp colours for paper surfacing, but more especially for the latter The strong staining ochres used for decorative paints are not often employed, owing to their much higher price and relative brownness. The usual procedure is to start with a good yellowish shade of ochre, cheap in price and fine in texture and either strike suitable basic colours direct on to it, or precipitate dye pigments on to it by chemical precipitation while the ochre is in suspension in the dye solution

RED LEAD (AND ORANGE LEAD)

The latter can be considered as a bright pure shade of the former, its more orange and brighter tone being mainly due to finer sub-division. As it costs appreciably more than red lead, it is only used for the brightest shades , its general properties can be considered as exactly the same as those of red lead, which owes its great utility as a base for bright scarlets and light reds, to its great covering power and weather-resisting properties in relation to its low cost. It is most useful in the paint trade for the production of good dense pale scarlets, vermilion shades, and up to deep geranium reds, but it cannot be profitably used to any extent in darker shades, owing to the chalky or muddy effect which would be obtained in these cases.

Red lead at one time had a bad reputation as a base, because of the great risk of " feeding " and " settling out " of paints and enamels made from colours on this base To-day most of this risk is eliminated by the introduction of special grades known as "non-setting red lead," and by the fact that varnishes and paint media are more generally made by scientific methods, and are therefore less liable to be of an unstable nature or to contain excessive free acids

The conditions governing the production of a good non-setting red lead are—

(*a*) *Percentage of PbO_2*—the nearer to the theoretical figure of 34 9 per cent in the formula Pb_3O_4, the safer the red lead. Commercial non-setting red lead usually contains 33·0 per cent PbO_2, while ordinary red lead may contain as little as 20 to 25 per cent PbO_2.

(*b*) *Particle size* The material in which particle size is extremely small gives the best results (see orange lead above)

The reason why this fineness of particle size helps the stability of oil paints in which the red lead is used, is most probably a question of suspension of particles Any serious tendency to settle, results in a high local concentration of lead oxide particles in proportion to oil or varnish where the settling has occurred, and once the action has been started it spreads rapidly throughout the mass

Red lead for use as a pigment base should therefore be of the special non-setting type, and should be examined under the microscope for particle size against a standard, and also analysed for actual PbO_2 content

Satin White

Satin white is a useful base for the cheaper kinds of pulp colours for paper, and is sometimes used for distemper lakes It is a mixture of calcium sulphate and aluminium hydrate, usually prepared by double decomposition from alum or aluminium sulphate and milk of lime

As this is a relatively cheap base, it is important when using it to verify that it does not contain excess lime or saline matter. This base has a fine white smooth appearance and is of great importance for paper surfacing.

ZINC WHITE

Zinc white is sometimes used alone or in conjunction with blanc fixe as an opaque basis for strong transparent yellows, such as those of the stilbene, pyrazolone and Hansa yellow series, and also occasionally to render deep heavy greens or blues lighter in shade and more opaque.

Lithopone is also used in this way and for the same reason.

SILICA

When a chemically inert base is required, and less opacity is desired than is obtained by the use of blanc fixe, silica flour of the finest whitest grade is a very useful base. The best grades cost only as much as good quality blanc fixe, and have approximately the same bulking value in oil as the finest blanc fixe and give more permanent suspension. At the same time, silica imparts far less opacity to the lake colours in which it is used than a corresponding quantity of blanc fixe

CHAPTER XV

PRECIPITANTS

SOME of the precipitates, formed in the "striking" of soluble dyes to produce an insoluble lake or pigment form, are at least in part, properly speaking, occlusions. In precipitating small percentages of blue or of yellow dyes on to Drop black or Carbon black in order to improve or modify its tone, there is no actual chemical precipitation. Again, in the case of the precipitation of basic dyes on a pure diatomaceous earth, occlusion only appears to enter into the question. With basic dyes on white earth and green earth it is generally supposed that the action is partly precipitation and partly occlusion or adsorption; for only part of the precipitated dye can be extracted with warm alcohol

(*a*) *Iron Silicate* In addition to the natural green earths (or Veronese greens), which show high affinity for basic dyes and some of which will precipitate up to 11 per cent of their weight of Malachite green, a natural iron silicate can be prepared which has a still greater affinity for basic dyes. This process has been used by Meister Lucius and Bruning for the production of Milori blue substitute from Methylene blue B. The formula given* is as follows :—

"Waterglass" (26%)	110 parts
"Methylene blue conc" (2% solution)	20 ,,
"Conc sulphuric acid" (diluted with water)	14 4 ,,
"Green vitriol" ($FeSO_4 . 7H_2O$)	20 8 ,,

This colour lake is claimed to be much faster to light than lakes from the same dye on natural green earth. The blue formed has the great advantage over Milori blue of being fast to lime

(*b*) *Resin soaps, tannates, tannic acid and synthetic mordants* are all used as precipitants for basic dyes and in the case of all except the tannic acid, complex salts appear to be formed These special precipitants, as well as green and white earths, are more fully referred to in Chapter XVI

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*H Wagner, "Die Körperfarben," p 20.

(*c*) *Alumina* In some cases finely suspended alumina functions as an adsorbing agent This is so when it brings about the "precipitation" of the last traces of otherwise too soluble dye lakes, as, for example, in rendering the precipitation of barium salts of Naphthol yellows and of Naphthol green B more complete.

(*d*) *Soluble metallic precipitants* are used chiefly in making various shade modifications of natural organic dye lakes, such as cochineal, madder root, etc Some of the most important are stannous chloride, ferric chloride, aluminium sulphate or acetate, calcium chloride or acetate, and barium chloride

1. *Calcium Acetate* is largely used in precipitating Permanent red lakes of the new Permanent red and Pigment red types

2. *Ferric Chloride* is only used in one connection to any extent, viz , the production of deep fast purple shades from madder or alizarin The purple produced is dull and heavy in shade, but is strong and very fast

3. *Lead Nitrate* is used as a precipitant in various different series, thus—

- (*a*) For Auramine yellow lakes on blanc fixe where green earth or white earth would give too dull a lake.
- (*b*) For practically all lakes made from the various types of Eosins
- (*c*) For several azo pigment dye lakes where the lead salt happens to have the most suitable properties, such as Helio red R M T.

4. *Copper Sulphate* is used in one or two special cases. When copper salts of simple azo dyes, from diazotised unsulphonated chlorotoluidines, e g , 3-chloro-*p*-toluidine, coupled with beta-naphthol, are prepared they are superior in brightness and general properties to the barium or calcium salts Copper salts are also used, and give good deep maroon shades Generally speaking the copper salts of pigment dyes, which are usable, are very insoluble and quite fast.

5. *Manganese salts* of one or two of the more recent pigment dyes have excellent properties, but (as with the copper salts) there are very few dyestuffs which give lakes of good shade and other necessary properties with this metal. Manganese salts are

also used as precipitants for a strong fast maroon, viz , Lake Bordeaux B N. (I G) In this case the aluminium salt of the dye gives a very deep dull maroon, whereas the manganese compound is much brighter and lighter in top tone, but still has a fine blue undertone It is unusual to find an aluminium lake deeper and fuller than that produced by heavier metals Aluminium is often used to obtain paler yellower shades of red lakes than those from lead, calcium and barium (compare Eosins p 202, alizarins p 231 to 237). The individual user should test lakes with all possible or likely metallic precipitants for his own information The older, commoner types of pigment dyes have been well explored in this way in the past, but there is more promise of varied and useful results in this field among the fast Pigment red and Azo rubine classes.

6 *Chromium* This is seldom used, but one example which has a definite use is the chromium lake of Gallo violet D. (By), an acid oxazine dye giving a dullish violet chromium lake, very fast to light and lime.

7 *Barium Chloride*. By far the commonest precipitant for the large range of acid azo dyes and for acid (sulphonated) dyes of the triphenylmethane series is barium chloride No special precautions are necessary when using this salt as a precipitant, except to use a relatively large excess over the theoretical and to ensure that a distinct excess of free barium chloride is present in the filtrate from the lake. The reason for this large excess is that the depth of shade, fastness to light, and insolubility of the pigment all depend on a complete conversion of the sodium salt of the dye into the barium salt Actually this 100 per cent reaction seldom takes place, for the heavy molecules of some of these azo pigment colours give only a slow and feeble reaction between their sodium salt and the free barium or calcium chloride A balance is therefore reached finally, depending on strength of solution, activity of the particular dye molecule in question, and relative proportions of sodium salt of dye to free barium chloride

Taking DM to represent a free dye molecule, the balance reaction is shown thus .—

$$2\text{DM Na} + \text{BaCl}_2 \rightleftarrows \left.\begin{matrix}\text{DM}\\ \text{DM}\end{matrix}\right>\text{Ba} + 2\text{NaCl}$$

Such colours as Lithol red and Lake red C require a good excess of the precipitant to give full deep shades and to ensure freedom from bleeding.

8. *Calcium Chloride* is used for many of the insoluble Pigment red lakes and for most of the Azo rubine and Permanent red classes. In the last range of colours it will often be found that on keeping they change to a duller yellower form, owing it is supposed to a slight absorption of water This can be obviated by *replacing* 20 per cent of the calcium salt used for precipitating the lake by *strontium chloride.* The resultant lakes retain their colour quite well in storage, and the shades are usually slightly improved by using the proportion of strontium salt given This is particularly useful with Permanent red 2B., and to a less extent with the B and 4B. grades

Whenever calcium salts are used, a great excess of the precipitant should be avoided and the lake must be thoroughly washed until all traces of soluble calcium salt are eliminated, otherwise the finished lake will always be hygroscopic, even if it has been satisfactorily dried and ground

9. *Stannous Chloride* is seldom used except in the production of special light shades of Madder and Cochineal lakes, being generally employed in conjunction with Alumina

Finally, in using barium, calcium and strontium salts as precipitants for soluble dyes, care should be taken to buy dyes whose saline content, if any, is in the form of sodium chloride. Glauber's salt used to facilitate filtering the dyes during their manufacture is quite permissible in textile dyes, but in lake making causes the production of a certain percentage of very finely-divided barium, calcium or strontium sulphate in the lake, and this gives the lakes a flatter, more chalky appearance. It also partly impairs the blueness of undertone in the case of red lakes. This is very noticeable with acid Ponceaux Most dyes sold for pigment or lake manufacture contain no soluble sulphates, Pigment scarlet 3B (see page 165) being an exception

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CHAPTER XVI

Lake Colours from Basic Dyestuffs

BASIC dye lakes furnish a range of somewhat fugitive colours, which are of a brilliance and purity of tone not obtainable with faster lake colours, so that they are still in constant use, in spite of their fugitiveness to light, and their tendency in many cases to bleed in water or in oil.

A further reason for their importance is that they furnish a series of brilliant shades covering the whole range of purple and reddish-violet shades to be found between a pure blue and a pure crimson This bright range cannot be filled by any other class of faster dyestuffs known at present.

Dyestuffs of distinctly "basic" properties are found mainly in the following chemical classifications :—

Diphenylmethane (Ketonimine) derivatives
Triphenylmethane „
Xanthene „
Azine „
Oxazine „
Thiazine „

The commercial products are generally the water-soluble hydrochlorides of the dye bases

These chemical classes also include dyes which are derived from sulphonated or disulphonated primary constituents and which, having acidic properties due to the sulphonic groups, require a metallic salt as precipitant For this reason, any such members are referred to in Chapter XIX on lakes from soluble acid dyes

Several examples of the best known of each of the above-mentioned classes are given on pages 197 and 198 together with some of their special characteristics. Fuller details will be found in "Die Korperfarben" (H Wagner, pp. 277—286)

Methods of Precipitation of Basic Dyes.—These are varied and the actual choice of method depends on the exact requirements for the particular lake to be made The main processes depend on the use of negatively-charged precipitants, some of which combine chemically with the basic dyestuffs, whilst others precipitate partly by combination and partly by adsorption

Adsorption by chemically inert bases is also utilised where no chemical combination is possible, but in the processes where both adsorption and chemical combination are involved, it is highly controversial as to how far the precipitation is due to adsorption and to chemical combination respectively

The best-known reagents for the precipitation of dyes of essentially basic character are—

(*a*) Green earth.
(*b*) White earth.
(*c*) Synthetic precipitants (formaldehyde condensation products, etc)
(*d*) Acid dyestuffs
(*e*) Tannic acid
(*f*) Tannin-tartar emetic
(*g*) Resin soaps.
(*h*) Arsenite and phosphate of alumina
(*i*) Inert adsorbent substrata

Several other methods can be used, but seldom come into general practice

All of the above methods are used and the bases or substrata are almost as varied The various methods are employed according to the special properties required of the lakes thus made

Green earth.—Green earth is the most generally used and the most important of the precipitating agents mentioned. It is a natural product of the "weathering" or breaking up of complex silicates, such as hornblende and augite The resultant green earth varies largely in composition according to its source. The quality and properties of the basic-dye lakes produced with different grades of green earth also vary enormously, and for this reason when purchasing it is of paramount importance to select and test carefully, by means of actual dye precipitation tests, before passing any particular consignment to the factory

The essential chemical constituent of green earth, suitable for basic dye precipitation, is a relatively high percentage of ferrous silicate, with a smaller percentage of aluminium and calcium silicates. Some potassium or sodium silicate is usually present The main sources of the best grades are Czecho-Slovakia, Cyprus, Monte Baldo near Verona, and The Tyrol. Some qualities are of a dull green shade, others have a distinct clean green appearance (as "Veronese Green"), while others are of a pale greenish or greyish yellow. The lake making properties cannot in any way be judged from this appearance, although any sample of decidedly dull heavy appearance, cannot be used for very pale bright shades Generally speaking the pale, distinctly greenish shades, containing a high percentage of ferrous silicate, are the best It must be particularly noticed however that some very pale earths contain certain organic and inorganic constituents, which precipitate a portion of the dye as a lake of very full heavy shade Often, a clean pale earth of unsuitable quality gives, with Malachite green, for instance, a much bluer dirtier shade than is obtained from a darker duller earth of suitable composition and properties

As this practical colour striking test is so simple and quick, it should always be carried out when passing any sample or delivery of green earth A standard dyestuff at a standard concentration should always be used for this test, taking care not to make too deep or strong a lake. A 2 per cent dye lake is quite suitable for readily detecting any marked differences.

It is generally accepted that the precipitation of basic dyes on green earth is largely due to adsorption, and this is to some extent supported by the fact that much of the original dyestuff can be extracted from a dry green earth lake by warm alcohol, and by the fact that dispersing agents, such as Turkey red oil, naphthalene-2 7-disulphonic acid, and ammonium acetate, have such a marked effect in improving the brightness and uniformity of shade

In all cases of precipitation by green earth, there is an appreciable percentage of the dyestuff which is assumed to be chemically combined, as it cannot be wholly extracted by ordinary solvent methods Given a really good quality of green earth, most basic dyestuffs yield lakes of the best all-round properties as regards shade and fastness, in this series. The two precipitants which give brighter and cleaner tones are resin soap and arsenite (or phosphate) of alumina, both of which, however, give lakes that are considerably more fugitive to light, and in some colours have a distinct tendency to bleed

The general procedure for making green earth colours is the same for all basic dyes. The green earth serves as substratum as well as precipitant, although some more opaque base may be added to give greater density, or to produce a paler and more opaque shade Alumina is sometimes added, and is indeed necessary when dealing with very soluble members of the basic dye series, or when using such synthetic precipitants as those mentioned in Class (c). In both cases the alumina is most efficaceous if used as a fine, freshly washed suspension, or better precipitated in the lake making process It acts purely as an adsorbing agent and reduces the solubility of the dye lake in water

Various processes have been described for producing basic dye lakes by rapid methods For the sake of cheapness in grinding and drying and also to reduce the loss of soluble dyestuff when producing lakes of fair concentration, methods have been used in which the dry green earth is mixed in a pan mill and the basic dye sprayed on to the earth as a very concentrated solution, either in water or alcohol, while mixing in the mill Deep heavy shades of moderate fastness are obtained by this method, but the shades are always far duller and the tendency to bleed greater than by a more rational wet process, with the dyestuff properly diluted and subsequently well dispersed over the whole of the substratum The essential factor in obtaining bright uniform lakes on green earth, assuming the latter to be a good quality uniform standard, is to keep the dyestuff well dispersed throughout the operation of striking. Points to avoid therefore are—

1. The use of any vessel or stirrer, which may have contained alkali in any form, and so would precipitate some of the free dye base from a basic dye solution.

2. The use of water containing too much free lime or ammonia, for the same reason as (1) The usual precaution in either case is to use a very small percentage of acetic acid (0.1 per cent) in all water employed for making basic dye lakes

3 Using the dye solution too concentrated or adding it too rapidly to the green earth

4. Failing to make use of efficient continuous stirring throughout the addition of the dye solution to the green earth.

If sufficient water be used to allow of the dye being used at not more than 3 per cent to 5 per cent concentration, according to its solubility, and if the green earth be well mixed up with hot water to a uniform, fluid consistency, no difficulty should be encountered in making a good product Some dispersing agent, such as Turkey red oil or naphthalene sulphonic acid, is necessary and this is preferably divided, one-half being stirred with the earth, the other half being added to the dye solution

With the less soluble members of the basic dye series, it is an advantage to use hot solutions (70° to 80° C) and to use hot water in the green earth suspension

Although apparently it is a very simple operation to dissolve a basic dye powder in hot water and add this solution to a substratum, the operation presents pitfalls for the unwary. Owing to the very dark solutions formed by most of the dyes, it cannot be easily determined when the whole of the dye has completely dissolved, and any undissolved specks of dye will completely ruin the lake produced. A standard method should be adopted for this dissolving process. A good method is to place warm water, 1 gallon for every 5 lbs. of dye, in a large earthenware or enamelled vessel, add the full quota of acetic acid and one-half of the Turkey red oil to be employed (see p 198) In this mixture, the dye powder can be readily reduced to a smooth paste, thus eliminating all imprisoned air, and clots of dry powder For such colours as Safranine and Victoria blue, which are poisonous light powders and which float on water and are therefore difficult to mix, the use of one-half of the dispersing agent is also an advantage in that the dye is more readily wetted

The dye paste is next dissolved completely by the addition of the remainder of the water, which is used almost boiling After a few minutes stirring, the solution is allowed to stand, and then added to the well agitated substratum, through a very fine muslin or flannel cloth to ensure that no solid dye particles pass into the batch As a further means of obtaining uniform and bright shades, the dye solution should be added fairly slowly with good stirring in order to avoid loss of dyestuff. When making heavy shades with the more soluble dyes, the operation must be conducted in a much more concentrated solution and using only warm water to dissolve the dye. The same care must be taken to ensure the complete absence of particles of undissolved dye, by efficient stirring and filtering the dye solution before use.

The same precautions as regards complete solution of the dye, careful progressive addition of dye solution to precipitant, and the avoidance by means of efficient stirring of localised agglomerations or localised precipitation, are equally important in the processes to be described in the following pages

White earth may be classified with green earth as it is very similar in constitution, but contains much less iron and being, as its name implies, almost white, can be used for pale yellow basic dye lakes (such as Auramine) which would be too dull on green earth

Tamol NN and Katanol. Tamol NN and Katanol are synthetic precipitants for basic dyes made by the I.G Both are sold in powder form ready neutralised with sodium carbonate The former is reputed to be a formaldehyde condensation product of naphthalene disulphonic acids, and the latter a thiophenol product These products have certain advantages over tannic acid and tannin-tartar emetic The proportions of Tamol or Katanol to be used with any particular dye should be regulated according to the maker's instructions.

The advantages are that the lakes produced are generally brighter, cleaner, and faster to lime than the corresponding tannin lakes The latter, however, are rather faster to light. In using Tamol, care has to be exercised to use less than the theoretical amount, and to complete the precipitation with a slight addition of aluminium sulphate This results in the formation in the mixture of freshly suspended aluminium hydrate, which acts as an adsorbent Excess of Tamol further decomposes the already formed normal Tamol lake. On the other hand Katanol in reasonable excess has no deleterious effect.

When good fastness to lime and water, with brightness of shade, are essential, these two synthetic precipitants are to be recommended, but when greater fastness to light is essential, and some degree of brightness, and fastness to water and lime, can be sacrificed, tannin or green earth lakes are to be preferred. The tannin precipitation, if carefully performed, gives the greatest fastness to light in most cases, but the lakes are still duller than those on green earth

Acid Dyestuffs as Precipitants Acid dyestuffs are very effectively used in some cases as precipitating agents for basic dyes Most of the satisfactory lakes which can be produced in this way, in which neither component tends to bleed out, and in which the combination gives a stable and fast product, are rather dull in shade Several good blacks, dark greens and dark blues can be made in this way They are very fast to most ordinary agencies. One exceptionally useful example of this type of product is Helio marine 2GL (By), a colour produced by the mutual precipitation of Methylene blue 2B. and an Acid alizarine blue The colour produced is an insoluble blue pigment dye sold as a dry powder, suitable for developing to ordinary pigment strength, by grinding in an edge-runner with a suitable base

Deep rich shades of maroon and mahogany lakes can be produced in the same way by precipitating Magenta with various acid Ponceaux on a suitable base. They are generally faster to light than either component

Tannic Acid Tannic acid is generally used in conjunction with tartar emetic as a basic dye precipitant The quantities of each have to be carefully adhered to and the weight of tartar emetic used must be at least one-half the weight of tannic acid Any excess of free tannic acid will give dull shades, which gradually turn duller during storage and even show a distinct yellowing or browning on long exposure, if the excess has been appreciable

Care must be exercised with all tannin solutions and with the lake batch throughout the process to guard against any accidental contamination with iron or rust at any stage, as the formation of almost black tannate of iron will be sure to dull the shade of the lake

Two typical lake batches are given below, using tannin tartar emetic These yield very strong transparent lakes suitable for lithographic work

1. *Methyl Violet Lake* 10 lbs of Methyl violet 2B. dissolved as already described (at 5 per cent strength) in water at 50°C is run into a vat containing 500 lbs. of 10 per cent alumina paste of 10 per cent strength, stirring meanwhile.

A solution of 14 lbs tannic acid in 30 gallons water at 30° C is slowly run in, stirring well, and then a solution of 8 lbs. tartar emetic in 20 gallons warm water is added Finally 1 lb of aluminium sulphate in 2 gallons of water is run in

After stirring a few minutes the lake is allowed to stand, then filtered and pressed This lake is very strong and yet transparent, but is not very fast to light

The only Turkey red oil used in this lake is ½ lb employed in the dye solution

2 *Magenta Lake* The procedure is exactly the same as for the Methyl violet lake, except that 12 lbs of tartar emetic are used for this dye in the same sized batch, i e. —

Magenta 2B powder	10 lbs
Alumina paste (10%)	500 ,,
Tannic acid	14 ,,
Tartar emetic	12 ,,
Aluminium sulphate	1 lb

This lake again is very strong and bright, but not fast to light. These two are typical examples of strong bright lakes used for cheap lithographic or decorative paper work.

A similar lake process to the foregoing is that in which tannin tartar emetic is used in conjunction with a more opaque base, in this case a simultaneously precipitated barium sulphate base This gives a very soft smooth lake of good brightness and opacity, for paper surfacing A typical colour is Brilliant green, made as follows —

Brilliant Green Lake. 30 lbs. alum dissolved in 40 gallons warm water (40° C). Add to this with good stirring 15 lbs. soda ash dissolved in 20 gallons water After stirring for 15 minutes, run in slowly a solution of 32 lbs. barium chloride in 30 gallons of water Follow this with a hot strained solution (60° C) of 5 lbs Brilliant green crystals in 12 gallons of water with ¼ lb Turkey oil and 1 oz acetic acid added The dye must *not* be added before the barium chloride or a hard final product will be obtained The barium chloride is used merely to produce the combined base, and not as a dye precipitant.

The final precipitation is effected by adding 5 lbs tannic acid dissolved in 12 gallons water, followed by 2½ lbs tartar emetic in 6 gallons water, both added slowly

The precipitation is effected throughout at about 40° C. The colour is simply filtered to as hard a cake as possible and dried at a low temperature

Another process giving slightly brighter lakes is that employing the same mixed base as just described and tannin as precipitant, but in place of the tartar emetic, flour starch is employed, to about twice the weight of tannin used

Resin Soap Lakes These are the brightest of all the ordinary basic dye lakes, but they are very fugitive to light as compared with the tannin lakes and often bleed in either water or hydrocarbons. In spite of this fugitiveness, they still have a distinct but restricted field as colours for bright decorative effects and paper surfacing, where exceptional brightness of shade is the only consideration. Examples of vivid, bright colours obtained by this process are those from Brilliant green crystals, Rhodamine B , Auramine O , etc

A typical process is given below

½ cwt W.W rosin is dissolved in 60 gallons boiling water, with 16 lbs soda ash. The clear soap is cooled to 80° C and 2 cwts of 10 per cent (washed) alumina paste stirred in The hot dye solution is next added, viz 6 lbs Rhodamine B in 15 gallons water at 80° C The whole mixture is stirred and maintained at 60° C , and a hot solution of 14 lbs barium chloride in 20 gallons water is slowly run in, while stirring vigorously The finished lake is allowed to cool down, with slow stirring, filtered and pressed, and dried at a low temperature in the vacuum oven

The process in which either arsenite or phosphate of alumina was used to produce bright but rather fugitive lakes for paper work, is scarcely ever used now and need not be further described

Adsorbent Agents as Basic Dye Precipitants Some special grades of almost pure, inert silica, such as diatomaceous earth, and certain relatively inert natural silicates, have a distinct adsorbtive affinity for most of the basic dyes, and will take up from 2 to 3 per cent of the most suitable dyes These inert earths are used to a limited extent in the production of weak, bright lakes, which, however, are not properly fast to water and still less so to spirit

Carbon black of various grades has a high adsorption power for many basic dyes—up to 12 per cent or more in some cases There is one practical application of this, viz , the use of *small* percentages, usually not more than 1/5th per cent on the total weight of black, of a suitable blue dye to enrich and enhance the blackness of smoke or carbon blacks Even a pure rich vine black may be much improved by impregnating the wetted black with the correct small percentage of a suitable pure blue Methylene blue 2B in some cases, while in others an acid dye (Alkali blue or Pure wool blue), is used for the best results.

In enriching the shade of natural ochres with yellow basic dyes, adsorption plays some part, but it is quite possible that chemical combination also is involved The use of basic yellow dyes for this purpose is not to be recommended, because ochres are so often used in water paints where there is a great risk of the yellow dye bleeding in the aqueous medium Furthermore, any such dye addition is very easily detected by extraction with boiling alcohol

Several other methods of precipitation can be used for basic dyes, such as casein emulsions, albumen, etc , but these are seldom, if ever, employed.

A special type of lake with a high percentage of dye may be prepared from basic dyes by precipitating with special silicious substrata For example, in a method patented by Eberlein and the Kochel Werke,* silicious minerals, colloidal aluminium silicates, or such prepared substrata as " Permutit," are used. The lakes are made at a high temperature, with prolonged boiling, and although the main combination between dyestuff and base appears to be due to adsorption, these lakes, even with a very high content of dyestuff, are reasonably fast to water and light.

A few well-known examples of each of the classes of basic dyestuffs mentioned on page 191 are given below as a guide

Diphenylmethane (*Ketonimine*) Auramine (this being the only member of the class in use)

Triphenylmethane. Malachite and Brilliant greens, Magenta, Methyl violets, etc

Xanthenes The several varieties of vivid red-violet shades—rhodamines

(These, possessing alkylated amino groups as basic characteristic, and a carboxyl group as acidic characteristic, will react as either basic or acidic dyes. The carboxyl group has no great influence on the light fastness in this case, but causes the dye to be more water-soluble and so the lakes are more prone to bleed in water.)

Azines. Safranines and Rhodulines are distinctly basic, giving bluish-red to violet-blue shades, and Induline bases are of blue to blue-black shades

In the graphic formula below for a typical Eosin (Eosin A. yellowish) the two hydrogen atoms marked $\boxed{H}$ are the two which *in the commercial Eosin are replaced by sodium* and subsequently by lead in the finished lake

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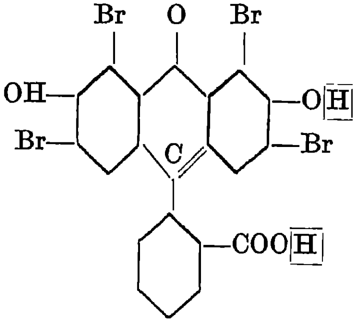
*H Wagner, Die Korperfarben, p 323



The remaining xanthene types, such as Phloxine and Rose Bengal, have the same essential structure, and only vary in the type and number of halogen atoms, as for instance

Erythrosine is tetra-iodo-fluorescein, Phloxine is tetra-bromo-tetra-chloro-fluorescein, Rose Bengal is tetra-iodo-tetra-chloro-fluorescein

Oxazines. Nile blues A and BB (Berlin), basic blues of the Gallocyanine type, giving fairly fast lakes, of deep greenish-blue tone.

Thiazines. Methylene blues B , 2B , and 3B The last gives a lake of pure Chinese blue tone.

CHAPTER XVII

LAKES FROM XANTHENE DERIVATIVES

Eosins, Phloxines, etc.

THE range of dyes produced from Fluorescein all being xanthene derivatives of an acid character, and containing no basic groups, are in a class by themselves The acidic groups are of two types, OH and COOH. The series gives lakes by precipitation with aluminium salts or lead salts, ranging from an orange scarlet to a bluish-red Arranged in this shade order they are—Eosins, Erythrosines, Phloxines, Cyanosines, Rose Bengal.

The lakes nearest to orange-scarlet in shade are obtained from the yellower shades of Eosin, in the form of aluminium salts, while the deepest blue undertones are found in the lead salts of Phloxines and Rose Bengal

This series yields lakes of extreme brilliance and clean pure tone, but unfortunately not very fast to light The simply prepared lakes, when not protected by varnish or other medium, are very fugitive In enamel colours, or under varnish or other medium, the fastness is notably improved and in the case of such shades as that from Eosin YS (B D) struck on orange lead, pigments of remarkable brightness are available, which are quite fast enough for use as vermilionettes for enamelling coaches, trams, &c The same types are also used for brilliant shades in linoleum, and for vividness of shade cannot be equalled by other and faster dyestuffs

A typical formula for an orange-scarlet shade of vermilionette is as follows —

Eosin 3Y. (B D) 60 lbs. dissolved in 150 gallons hot water in a mechanically stirred vat is slowly precipitated by the addition of a solution of 48 parts aluminium acetate in 50 gallons hot water After stirring a few minutes, a suspension of well-washed alumina paste, equal to 60 lbs dry weight, is stirred in The colour is washed, filtered and dried in the ordinary way.

A slightly less orange scarlet is produced by precipitating with 60 lbs to 70 lbs lead acetate in place of the aluminium acetate These two lakes are not very opaque, but are very strong and bright, and suitable for printing ink or lithographic work A still more orange and opaque type of pigment than the above, suitable for paints, is obtained by using 2 cwts or so of orange lead, in place of the alumina The order is then reversed, that is to say the dye solution is run slowly into the orange lead, previously " pulped " in water, finally precipitating by the addition of the solution of aluminium acetate or lead acetate.

The bluest reds are obtained in the two respective types, transparent for printing ink colours or opaque for enamel and paint colours, from Eosin 2BS. (B D) or Rose Bengal

Pure lakes of the medium to bluish-red shades, on alumina bases are sold as Geranium reds

Imitation Vermilion

A rich shade, equal to deep vermilion in tone and strength, is made by the following process —

1 cwt orange lead, ground to a pulp with 2 gallons water in a pan mill

A solution of 8 lbs Rose Bengal in 6 gallons of hot water, after carefully straining to ensure that no dyestuff remains undissolved, is slowly worked into the pulp orange lead while the mill is running This is followed by the gradual addition of 24 lbs lead acetate dissolved in 4 gallons hot water

After well mixing, the thin mixture is transferred to a clean tub and washed It is then filtered and dried This is essentially an opaque strong pigment for paint or enamel work

Phloxines give even brighter bluer undertones, but generally speaking are rather less fast to light than the yellower Eosins or the similar shade of Rose Bengal

CHAPTER XVIII

"FANAL" AND "BRILLFAST" COLOURS

REMARKABLE variations in the fastness to light of members of the "basic" dye groups were noticed many years ago, for example, in the different fastness to light of lakes from one given dye, but precipitated respectively by green earth, tannin, or resin soaps It was not considered possible to make any revolutionary change in this respect, until it was noticed that a dye such as Malachite green, dyed on to tannin mordanted cotton, although faster than a simple lake from the same dyestuff, would give a faster shade when dyed on to cellulose acetate silk, a fact first observed about 15 years ago

Meantime experimental work was being carried out extensively in Germany, culminating in the patenting of the Fanal colour processes by the Bayer Co , in 1923 and onwards. The essential feature of these colours is the precipitation of a dyestuff having basic characteristics by means of complicated acids (phospho-molybdo-tungstic acid, and silico-molybdo-tungstic acid) An early patent was taken out by the Bayer Co , B P. 143,242, (1920) in connection with textile dyeing The present day range of remarkably bright fast Fanal colours is the result of processes and improvements described in the following patents :—B.P 216,486, Nov 27, 1924, B P 257,148, Aug. 26, 1926 , B.P. 265,032, Feb. 3, 1927 , B P. 270,750, April 5, 1928 ; B P. 275,943, Sept 20, 1928 ; B P. 275,969, Mar. 8, 1928 ; B P. 292,253, June 18, 1928

The above specifications are very interesting and show that a great amount of work has been done since the original patents were taken out No 270,750, for instance, deals with the processes by which Fanal colour lakes are treated under pressure in an autoclave, and their fastness to light and alkalis in most cases enhanced

No 275,943 describes the production of fast colour lakes from colourless aromatic compounds (such as diphenylmethane derivatives) by treatment with phospho-molybdo-tungstates

The latest types of Fanal colours, which are obtainable commercially, are in the form of the pure compounds of the complex phospho-molybdo-tungstic acid with the dyestuff, and are mostly sold as insoluble pure lakes in powder form They may be developed by grinding in the edge-runner mill with the desired substratum, and when required for lighter shades may be ground up with zinc oxide or lithopone They are of very great tinctorial strength and of remarkable fastness to light Most of them are quite fast to water, to lime and to oil Some of them have a slight tendency to bleed in oil or spirit, this tendency being most marked in the case of the reds and violets made from Rhodamines This point must be remembered in using the Fanal colours in oils or spirit Some of the most useful shades are given below with the name of the dyestuff from which they are reputed to be made

Fanal yellow G	(Auramine O)
,, yellowish-green GB	(Auramine and Blue green (Brilliant green)
,, Bremen blue	(Unknown)
,, blue B	(Victoria blue B)
,, blue LBB	(Brilliant wool blue F F R.)
,, rose	(Rhodamine 6G)
,, violet L4B extra	(Acid violet 4B)
,, violet R	(Methyl violet)
,, red 6B	(Rhodamine B)

“ Brillfast ” Colours

A still larger range of the same colours is made under licence, in England, under the name of “ Brillfast Colours.” It is claimed for these latter that they have less tendency to bleed in cellulose solvents than their original counterparts, and according to tests carried out by the author, this claim is well justified, so long as the solvent mixtures used are free from alcohols

CHAPTER XIX

LAKES FROM SOLUBLE ACID DYES

Lakes from soluble and slightly soluble dyestuffs of acid character by precipitation with metallic precipitants

THIS class includes, apart from the Eosins which have been treated as a separate class in Chapter XVII, many and varied types of acidic dyestuffs

One class which naturally follows the basic dyes and the Eosins on constitutional grounds, is that comprising the dyes of the triphenylmethane and azine series which are made from sulphonated constituents and therefore are "sulphonates of basic dyes," although not made by directly sulphonating the basic dyestuffs A basic dye which is commercially converted into an acid dye by direct sulphonation of the dyestuff (with Oleum), is Magenta, which is so treated to produce the well-known Acid magenta The dyes of the series above mentioned all yield lakes by the simple process of precipitating from their solutions with barium chloride. They all contain sulphonic groups (usually one, sometimes two and seldom more) In a few cases tin salts are used as the precipitant, but nearly all are generally produced as barium salts. All are soluble in water, while a number of them are rather too soluble and give lakes which tend to bleed in water The method of preparation of these lakes only varies in the amount of precipitant relative to dyestuff (varying from 100 per cent to 200 per cent), and the type of base used as a substratum Most pigments of this range are vivid in colour and fugitive to light Their chief use is in making cheap, bright lakes for paper-surfacing or for poster and lithographic printing, where brilliancy is essential and fastness to light of secondary importance For paper surfacing, the dye is precipitated on a smooth easily spreading base of good capacity, such as blanc fixe-alumina, satin-white, etc. When the lakes are required for printing or lithographic work, the dyes are precipitated on a base of pure alumina, or alumina with blanc fixe or china clay in smaller proportion, the base being in any case fine and transparent in order to keep the shade deep and rich

The only formulæ which it appears of interest to give here are two typical ones for rather soluble dyes of this series, in which alumina-blanc fixe is precipitated, in a very fine form, during the lake making process By this means the precipitation is much more complete and the tendency to bleed in water or spirit is less, owing to the adsorbent action of the finely-divided alumina This is an essential procedure with excessively soluble dyes (See Naphthol green, p 208)

(1) PALE GREENISH-YELLOW FROM QUINOLINE YELLOW S

To 3 lbs potash alum in 3 galls water add—
1½ „ soda ash „ 2 „ „

This is carried out at 60° C and then the dye solution as under is run into the base so prepared ·

1 lb Quinoline yellow S in 5 galls water
Stir well for 10 minutes and add—
(a) 5 lbs barium chloride in 5 galls water
(b) 1 gallon 10% alum solution, then—
(c) Slowly, ½ gallon 5% soda ash solution

The lake is washed and dried in the usual manner

(2) A COMPOSITE GREEN LAKE FROM QUINOLINE YELLOW S AND DISULPHINE BLUE V.

By exactly the same method, using the quantities below

Alum	3 lbs	as 10% solution
Soda ash	1½ „	as 7½% „
Quinoline yellow S	¾ lb	as 2½% „
Disulphine blue V	¼ „	
then—		
Barium chloride	5½ lbs	in—
Water	5½ galls	then—
Alum (10%)	1 gall	and finally—
Soda ash solution (10%)	½ „	

This yields an exceedingly brilliant pale green lake, but of very poor fastness to light

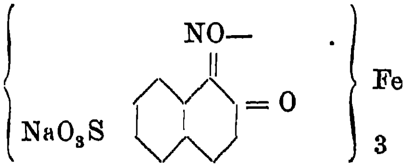
NAPHTHOL YELLOW S

Naphthol yellow S is a dyestuff of a totally different class 2 . 4-dinitro-α-naphthol-7-sulphonic acid, but has the same general properties of great solubility and only moderate fastness to light. It is, therefore, converted into a lake by the same method as the above The lake is of good middle chrome shade and rather faster to light than Quinoline yellow S It has a decided tendency to bleed in water and therefore is restricted in its use

NAPHTHOL GREEN B (see also p 167)

This is a dyestuff of quite a different class It is actually a nitroso colour, made by linking three molecules of beta-naphthol-6-sulphonic acid (Schæffer Acid) together after converting them into the nitroso compound

The linkage is effected by ferric iron, as shown in the formula below ·



A description of this colour and lakes made from it is included here, as it is one of the many dyes which form lakes rather too soluble in water It therefore needs special methods of precipitation, in the same way as Disulphine blue V and Naphthol yellow S just described

A useful practical formula for Naphthol green B. lake is as follows —

(*a*) Prepare a solution of 32 lbs aluminium sulphate (18% Al_2O_3) in 30 gallons of water at not above 20° C

Add to this with good stirring

(*b*) A solution of 4 to 6 lbs soda ash in 5 gallons of water—sufficient must be used to produce a very faint permanent cloudiness in the mixed solutions of (*a*) and (*b*)

To this mixture add gradually with good stirring a cold solution of

(*c*) Naphthol green B. (powder) 20 lbs in 20 gallons water.

Then add

(*d*) Barium chloride	50 lbs
Water	40 galls

Stirring well

Finally stir in a solution of 32 lbs soda ash in 59 gallons water

The lake is washed once, filtered and dried at a moderately low temperature

A more reduced quality is best prepared by adding a quantity (as required) of fine amorphous silica (Milowite) between stages (*c*) and (*d*)

The lake of this colour is very fast to oil, spirit, alkalies, and heat. It is not fast to mineral acids. It is successfully used in printing bank notes and also as a tinting colour for india-rubber

HANSA GREEN (As E P. 248,487)

As the very useful green dyestuffs possessing reasonable fastness to light and yielding bright lakes, are of rather different constitution from the dyes of the main classes adopted for lake making purposes in this book, they do not readily fall into line and for this reason have been included here Hansa green is a soluble dyestuff of the azine class and is prepared by the oxidation of suitable naphthylenediamine chloro derivatives with ferric compounds

It forms bluish-green lakes of excellent fastness to light, water and lime. These lakes are much less soluble than those of Naphthol green B and brighter, but not quite so fast to light The method of precipitation is just the same as for the various types of lakes made from soluble acid azo dyes

PIGMENT GREEN B. (see p 167)

Is an insoluble dyestuff of the " nitroso " class, and therefore a similar type to Naphthol green B. It has no lake-forming properties (i e , it does not react with metallic salts to form a metallic compound of the dyestuff) It is higher in price than Naphthol green B but in all general fastness properties is superior to the latter It has one slight disadvantage in use as a pigment, viz., that it turns very slightly browner in shade on long exposure to light

ALTERNATIVE METHODS FOR PRECIPITATING SOLUBLE ACIDIC DYES

1 A transparent blue lake, deep and bright in tone, is made by precipitating a suitable dye on to alumina base by means of tin salts

2. The lake may be made by a combined precipitation of Glauber's salt followed by barium chloride, in a mixture of the dye solution with alumina base in suspension.

3. The dye solution may be stirred into a suspension of alumina and precipitated with barium chloride only.

4. The same dyestuff solution may be mixed with blanc fixe or barytes in suspension and precipitated with barium chloride.

Methods 1 and 3 give a transparent lake suitable for glazes or lithographic work, method 2 gives one suitable for paper surfacing, and method 4, a more opaque pigment suitable for paint The above methods are suitable for use with Alkali blue and similar dyes. Alkali blue is so called because woollen goods when dyed with this are heated in an alkaline solution of the dye, giving a colourless or "leuco" dyeing, which develops to the full blue on immersion of the wool in weak sulphuric acid. The dye is actually acidic in character, being a mixture of sulphonates of triphenylmethane derivatives.

A similar, and still wider variation of method, is applicable to all classes of the simple water-soluble acidic dyes, when converting them into lakes, according to the physical properties and type of base required The above examples suffice to illustrate these differences, and other modifications can be made readily by the individual manufacturer to suit his particular requirements

LAKES FROM SOLUBLE ACID AZO DYES

Of all the soluble dyes used for lake making, by far the most important are the acid azo dyes of which there are many of the water soluble, or only slightly water soluble types Most of these are produced from the chloro, nitro, carboxy or sulphonic derivatives of aniline, toluidines, xylidine, and α-and β-naphthylamine diazotised, and coupled with beta-naphthol or its carboxy-derivative (beta-oxynaphthoic acid—see p 73) Of the enormous number of combinations possible in this group, the only ones of practical importance to the lake maker are couplings of diazotised aniline and toluidine derivatives with beta-naphthol and oxynaphthoic acid Some of these yield very bright lakes of excellent fastness to light, as for example :

ANILINE DERIVATIVES

Aniline	yielding	+Ponceau 2G
p-nitroaniline	,,	Autol red* or Para red
2 4-dinitroaniline	,,	Permanent scarlet 2G *
2 · 4-dinitroaniline-6-sulphonic acid	,,	△Permanent red B
aniline-2-carboxylic acid (anthranilic acid)	,, ,,	Lake red D * and Pigment scarlet 3B.
o-chloro-*p*-nitraniline	,,	Permanent red R. (A G F.A.)*
p-nitroaniline-*o*-sulphonic acid	,,	Lake red P *
4 5-dichloro-*o*-nitroaniline	,,	Lithol fast scarlet G *

TOLUIDINE DERIVATIVES

p-nitro-*o*-toluidine	yielding	Pigment orange R *
m-nitro-*p*-toluidine	,,	Helio red R L *
p-toluidine-*m*-sulphonic acid	,,	△Permanent red 4B
p-toluidine-*m*-sulphonic acid	,,	†Helio Bordeaux B L.
2-chloro-5-aminotoluene-4-sulphonic acid	,,	Lake red C* and △Lithol rubine G
3-chloro-2-aminotoluene-5-sulphonic acid	,,	Lithol red G G * (Hansa rubine 2G)
m-toluidine-4-sulphonic acid	,,	Helio red R M T *
6-chloro, 3-aminotoluene	,,	△Permanent red 2B
(Meta) xylidine	,,	+Ponceau 2R
Beta-naphthylamine-1-sulphonic acid	,,	Lithol red R *

*=Beta-naphthol combinations.
+=R. salt
△=Beta-oxy-naphthoic acid
†—Alpha-naphthol-5-sulphonic acid

It can be seen from this representative list that those dyes which yield the lakes fastest to light have almost invariably—

1 Either no acidic substitution in the amino component, or else the most strongly acidic substituent in this component is in the ortho position to the group

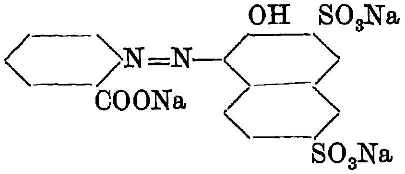
2 The most strongly acidic substituent, if any, in the naphthol component, is in the 3 position

3 The most favourable condition, viz an unsulphonated naphthol component, with a carboxyl group in the 3 ortho position (Beta-hydroxynaphthoic acid, see page 73)

It is important to note that a carboxyl group in the ortho position to the azo-linking in the finished dye, or in the 3-position in the naphthol residue, without exception, imparts great fastness to light in the finished lake Simple illustrations of this are—

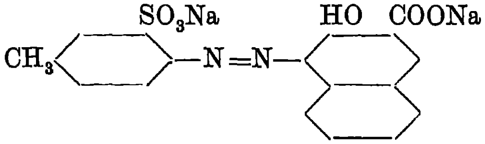
Pigment Scarlet 3B.

Carboxyl Group in Benzene residue



Permanent Red 4B

Carboxyl Group in the Naphthol residue



In addition, the Permanent Red 4B colour has its only sulphonic group in the ortho position to the azo linking—this being by far the most favourable position for a sulphonic group in the residue of the amino compound

Carefully prepared lakes from either of these two dyestuffs possess remarkable fastness to light.

" Permanent Reds "

An important subdivision of the acid-azo dyes is the small range known under the English names of Permanent reds B , 2B , 4B , 6B , and having various " Rubine " designations in Continental literature (the bright red F4 RL (I G) is known as Permanent red) All of these are manufactured from diazotised derivatives of aniline or toluidine, coupled with beta-oxynaphthoic acid. These give with barium, strontium, or calcium, lakes of scarlet to crimson shades, which are very fast to light and to lime, and possess in each case a splendid bluish undertone A deep bright Bordeaux shade is obtained from the dyestuff Lake Bordeaux B (I G) which is a derivative of alpha-naphthylamine coupled with beta-oxy-naphthoic acid

Permanent red 2B. is only partially soluble in water and is usually sold in wet paste form. The lakes of this and similar dyes, which give the brightest and best undertone, are the calcium lakes. The barium lakes, which are less blue in undertone are also used Unfortunately the calcium lakes of Permanent red 2B and 4B are slightly hygroscopic and absorb moisture on standing, at the same time changing to a duller and yellower shade The only means of overcoming this serious fault is to make a combined calcium-lead salt or a calciumstrontium salt of the dye Lakes made by this method do not turn yellow or absorb moisture on standing, if they are carefully made and well washed before drying. Yellowing of shade usually only found in the lakes made at 210° F , when the full bluish shade has been obtained. The mixed calcium and strontium lake gives the full blue shade when struck at 210° F If, however, a yellower shade is desired, the precipitation of a simple calcium lake may be effected at 100° F. which gives a yellower lake that will remain quite unchanged in stock

The following method for Permanent red 2B. or Permanent red 4B. is for a pure " 100 per cent " metal sale of the dye In both cases the product gives a rich, full-bronzed top tone for off-set printing lakes

10 lbs dry dye (Permanent red 2B or 4B , as the case may be),
or equivalent in paste

Boil this at 212° F with 140 gallons of water While stirring, run in the following mixed solution :—

11 lbs pure Calcium chloride crystals ($CaCl_2$ $6H_2O$)
3 lbs pure Strontium chloride crystals ($SrCl_2$ $6H_2O$)
dissolved in 15 gallons boiling water

Stir, at 210° to 212° F for 10 minutes. Turn off the steam and stir slowly for 1 to 2 hours After thoroughly washing, dry at 180° F.

The product is an " off-set " or " reflex " printing ink lake. It may also be used for reducing to a weaker, more opaque lake or pigment for paints, etc , by dry grinding with blanc fixe or barytes

The barium lakes of these two dyes are rather lighter and less blue in shade, but are quite stable when prepared

Permanent Red 4B. Lake

A printing ink lake of fine soft texture and brilliant over tone is produced by the following method :—

10 lbs	Permanent red 4B (dry)
	dissolved in—
50 gallons	Water at 120° F.
	containing 2 lbs acetic acid

To the above solution, add with fast stirring the following mixed base :—

5 lbs	Calcium chloride crystals in—
6 gallons	Water at 150° F
	to which has previously been added—
(*a*) 2 lbs	Soda ash in—
2 gallons	Hot water
(*b*) ½ lb	Barium chloride in
1 gallon	Water.

After stirring for 10 minutes, the batch is heated to 200° F. for ½ hour and then filled up to a bulk of 300 gallons for washing The top liquor must not show any free acid, but must contain excess calcium Add a few gallons of clear lime water to the second wash water, then continue washing with plain water until free from saline matter (taste) Dry at 180° F

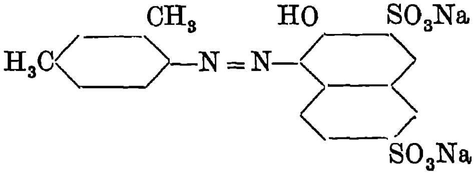
CHAPTER XX

LAKES FROM SOLUBLE AZO DYES

THIS classification is adopted to describe those lakes which are produced from clear dye solutions by simple precipitation with a metallic salt, this being in the majority of cases barium chloride, although in a number of cases calcium chloride and occasionally aluminium, lead or chromium salts are used. This covers a wide range of dyes from those derived from simple diazotised aniline sulphonic acid combined with beta-naphthol (Orange II) to those made from substituted naphthylamine derivatives combined with naphthols also containing several substituted groups Many of the more highly substituted lakes are actually " Pigment Reds " or " Azo Rubines," and as such have already been described in Chapter XIX.

The simple combinations with very few substituted groups are usually orange to scarlet shades as, for example, metanil yellow from beta-naphthol and metanilic acid, (yellowish orange lake with barium chloride), orange II from sulphanilic acid (reddish orange lake with barium chloride). These two dyes have only two substituted groups in the complete dye molecule, apart from the diazo linking (OH and SO_3H).

Further on in the same series are Ponceau 2G (orange-scarlet lake with barium chloride) containing three substituted groups (OH, SO_3H, SO_3H), and Pigment scarlet 3B. (deep reddish-scarlet lake with barium chloride) and Ponceau 2R (light crimson lake with barium chloride) the former containing four substituted groups and the latter five apart from the azo linking (Pigment scarlet 3B) structural formula on p 212 and Ponceau 2R structural formula as shown below —



(The above formula illustrates the fastest, most insoluble, and brightest type of Ponceau 2R, viz, that obtained by using pure meta (1 2 : 4)-xylidine) When the dye molecule is made heavier than that of this last-named dye, for example by using two naphthalene nuclei instead of one benzene and one naphthalene nucleus, as is the case in Ponceau 2R, then the lake from the resulting dyestuff is much deeper and "bluer" in shade, as for example lake Bordeaux B (deep bluish-crimson shade) made from alpha-naphthylamine and R. salt In this case there are only three substituted groups (OH, SO_3H, SO_3H). The increase in weight and complexity of the dye molecule generally has more influence on deepening and "blueing" the shade than an increase in the number of substituted groups The actual nature of the substitution and its orientation in the molecule gives rise to very wide differences in the colour of resulting dyes and lakes

The majority of simple acid azo dyes which can be obtained by coupling diazotised aniline or toluidine and their sulphonic acids, with beta-naphthol sulphonic acids, as well as those from diazotised alpha-naphthylamine and its sulphonic acids coupled with beta-naphthol or its sulphonic acids, give light scarlet to deep Bordeaux shades of red Most of these have been in commercial use from time to time as wool dyes Although a great number of the theoretically possible combinations yield bright, cheap products, relatively few of them are in regular use to-day as wool dyes because as a class they are rather fugitive to light and have been superseded by other dyestuffs The number of these dyes suitable for lake making is very much less Most of the bright clean shades which contain two or more sulphonic groups in the molecule have two great defects from the lake maker's point of view (1) Lack of fastness to light (2) Too great solubility in water, even as barium or calcium salts. The two following examples illustrate this —

(*a*) The bright bluish red Ponceaux from *m*-xylidine and beta-naphthol trisulphonic acid 3 6 8

(*b*) The equally bright crimson-maroon from beta-naphthylamine 8-sulphonic acid (Badische Acid)

Both of these are very brilliant colours and low in cost, but owing to their relative fugitiveness to light and their inability to give really insoluble metallic lakes, they are of little use for lake making, except for "topping" or brightening duller shades.

Among the dyes, which are of good fastness to light, but which fail as lake colours owing to the too great solubility of the metallic lakes, two may be mentioned :—

(*a*) Diazotised xylidine coupled with beta-naphthol-8-sulphonic acid (Bayer Acid)

(*b*) Diazotised naphthionic acid (alpha-naphthylamine-4-sulphonic acid coupled with Bayer Acid (see above).

These contain respectively 1 and 2 sulphonic groups in the dye molecule, but, owing to the great solubility conferred by the 8-sulphonic acid group, are useless as lake colours They are both, however, very brilliant bluish-reds of the Ponceau type and are fairly fast to light, and are used for wool and for paper pulp.

The simple acid-azo dyes do not as a whole give lakes of such great opacity and tinctorial strength, as those of the partly soluble class, such as Lake red C, Lithol red, Lake red P, etc In general, the undertone of the barium lakes of the Ponceau class of dyes, is much nearer to the top tone of the lake, than is the case with the Lithol red type This smaller divergence in under and top tone is of distinct advantage when blending colours to deepen or richen them, as there is thus less risk of dulling or browning the resultant shade For example, Ponceau 2R barium lake, which has a pure deep crimson top tone, without excessive blueness of undertone, may be used very successfully for lightening or brightening the shade of deep maroon and Bordeaux lakes, whereas another type, with extremely blue undertone, such as Helio Bordeaux B L would give a dirty shade if used for the same purpose

The preparation of lakes from this class of dyes is fairly simple, but as with all other colour processes, there is need for careful control of all physical conditions, and the establishment of standard methods in laboratory and works This is of course necessary owing to the fact that small variations in physical conditions (concentrations, temperatures, rate of precipitation and stirring, and duration of final heating or boiling) give rise to wide variations in shade and other physical properties of the product

Another factor which plays a part in this " double decomposition " type of reaction is " balance or reversible reaction," a factor very often overlooked When causing a " double decomposition " of most ordinary metallic salts by mixing in correct equivalent proportions, the reaction is of the following type —

$$BaCl_2 + 2\ NaOH = Ba(OH)_2 + 2NaCl.$$

Here there are two reacting substances which interchange their " metallic " and " acidic " radicles, two fresh products being formed with no subsidiary product This is the type of reaction entered into by the sodium salt of a simple acid azo dye, in lake making In the simple example of two metallic salts, just given, the reaction is generally assumed, for all practical purposes, to proceed to completion, and to be almost instantaneous In the case of the reaction between an acid azo dye sodium salt (for example Ponceau G) and barium chloride, if the retical equivalents of the two be taken, at the usual (say 10 per cent) concentration, or less, the reaction is relatively slow. In the cold its progress can actually be watched after mixing has taken place and the reaction does not attain 100 per cent interchange. In the case of dyes of high molecular weight and a complicated structure, the reaction is in some cases very slow, and only proceeds smoothly and completely in hot solutions. The " balance reaction " is illustrated in the following equation —

$$\overset{(W)}{\text{2 Ponceau G (sodium salt)}} + \overset{(X)}{BaCl_2} \rightleftarrows \overset{(Y)}{\text{1 Ponceau lake (barium salt)}} + \overset{(Z)}{2NaCl}$$

The explanation of this rather empirical illustration is that after a certain concentration of sodium chloride has been reached, the reaction proceeds also in the reverse direction, until a stable equilibrium of the four compounds W, X, Y, Z, is reached Y is the main insoluble product, but never formed quite completely If then the above situation is made still more unfavourable by the presence of large quantities of sodium salts (which would be the case when precipitating barium lakes direct from a dye made in the pigment colour works, without first pressing out the mother liquor), the excess of barium chloride required will always be much greater, quite apart from any excess required to precipitate soluble sulphates or carbonates, if any be present.

In the normal case of dyes bought as dry powders, or in using press cakes of " salted-out " filter-pressed dye, there is still a necessity to use a distinct excess of barium chloride.

With normal dye-powders, *free from sulphates* this excess will be calculated on 100 per cent dye content equal to ⅛ to ¼ of an equivalent excess This will mean that a moderate excess of barium chloride passes into the wash waters, but this is necessary if the reaction is to be stabilised and complete Otherwise the lakes may not be uniform in shade and strength, and will probably bleed unduly in water.

The effect of this balance reaction may be clearly seen by taking a series of 5 per cent solutions of any given acid dyestuff, and adding to each of the series gradually increasing percentages of sodium chloride solution If each of these dye solutions be struck with one equivalent of barium chloride in solution, the partial "balancing out" of the barium by the sodium chloride can be clearly shown in the results obtained

A further and equally important point is to use only dyes and dye pastes for lake making, which are free or practically free from soluble sulphates (see exception, page 166) This is very necessary with the simple Ponceau dyes, and any others which do not give very opaque lakes, the reason being that anything more than a trace of soluble sulphates, on reacting in such weak concentrations with the barium chloride used to precipitate the dye, will form barium sulphate in an extremely fine state of division, and this will give a flat milky top tone to the lake With still larger percentages of soluble sulphates, such as might be present in paste dyes, or in a dye solution or suspension made in the pigment works, a serious chalkiness of top tone and loss of blueness in the undertone will inevitably result Therefore the following safeguards should be used —

1 In making Ponceau and similar dyes from R. salt containing soluble sulphates, the dye when made must be "salted out" with sodium chloride and pressed to a cake in order to remove undesirable free sulphates

2 When buying dyes of this type, which may possibly have been manufactured also for use as wool dyes (in which case they probably contain sodium sulphate used in the salting out and standardising processes), tests should be made or else it should be specified when ordering that the dyestuff is to be free from soluble sulphates Comparisons can easily be made to show these differences by making a lake from sulphate-free Ponceau with 1¼ equivalent of barium chloride, and then repeating the experiment using the same dye and the same method, but

adding to the dye solution 1/10 equivalent of sodium sulphate In the latter case the top tone will be chalkier and the undertone less bluish in shade

Only one typical works method (for Ponceau 2R) lake is given below ; other lakes of this series are scarcely worth describing in detail as they do not form a really valuable class and the various dye manufacturers give full details for the precipitation of these soluble azo dyes

As regards the precipitant, important factors to note in making lakes from both the soluble and partly soluble type of acid azo dyes are—

(1) The rate of addition, (2) concentration and temperature of the solution, and (3) temperature of the dye solution *at the time of adding the precipitant.*

Once these factors have been standardised they should be adhered to most carefully The temperature of the dye solution when the precipitant is added, is of great importance and in many cases materially affects the result, irrespective of the final temperature reached, or duration of the final heating or boiling The greatest variations appear to occur with calcium lakes. These are points which must be settled by the individual worker The previous notes on " boiling up," agitation, etc , should be referred to for further safeguards necessary to ensure a uniform result It may be said that generally a temperature between 70° and 90° C is the best at which to add the precipitant.

If any one process has been successfully run on a certain scale, it cannot, however, be assumed that with a larger batch exactly the same result will be obtained by merely repeating all the conditions

In the first place it is very difficult to provide for the same rate of heating up or of precipitation of a larger batch , secondly, unless cooling coils be used, the rate of cooling down after boiling is very much slower A third factor which sometimes plays a part, is the question of the weight or pressure at the lower layers of a bigger batch, and the different conditions of " mass reaction " which obtain These variations may not actually affect the result of a smaller, successful process, but they must be considered as quite possible causes of error, when materially increasing the scale of any lake-making operation

CHAPTER XXI

LAKES FROM SLIGHTLY SOLUBLE AZO DYESTUFFS

MOST of the difficulties to be encountered in using dyes of this class for lake making, have already been referred to in the chapter on dye coupling (see pages 144 to 169).

As the dyes are only sparingly soluble in water, even at the boil, it is more difficult to ensure a standard and uniform reaction between the dye and the precipitant Although the precipitant is sometimes added to the cold, or merely warm dye suspension, it is a practice to be avoided if at all possible, unless as in the case of Lithol red and other similar lakes, it is desired to make two shades, one by cold precipitation and another (usually deeper) by precipitation at the boil When carrying out the former operation, it is essential to give the dye paste a thorough stirring in the water in order to ensure as complete dispersion of the dye particles as possible, before adding the precipitant For the same reason, in the cold precipitation, a little extra Turkey red oil should be stirred in with the dye before precipitating, and stirring should be continued over a long period to ensure complete interaction Very often a "cold" precipitation may be carried out at 30° to 40° C. without altering the shade, and if this can be done, it will be much more rapid and certain than if carried out at 15° C.

Even with all these precautions, there is always a greater risk of a tendency to bleed in oil, with a lake "struck" from slightly soluble type dye pastes, and finished in the cold, owing to the less vigorous reaction between the metallic precipitant and the dyestuff, at the lower temperature, and also to the less complete dispersion or subdivision of the dyestuff than when boiling. Most of the cold struck lakes of this type are rather paler and sometimes brighter in shade than those made at the boil, but are often liable to variation and changes of shade in drying They are usually less fast to light than the same type "struck" at 90° C and subsequently boiled

In making lakes from any dye of this class, it is best to precipitate at 90° C or 95° C. and then boil for 10 to 15 minutes, temperatures being checked by thermometers and not by apparent ebullition, which may not be due to actual boiling, especially if any bicarbonate of soda be present, as may be the case when using freshly made dye pastes, produced in the pigment works.

As a rule the proportion of barium chloride used in precipitating most of the paste (semi-soluble) azo dyestuffs, is a weight equal to the pure dyestuff content of the paste taken, e g., 60 lbs. of 20 per cent paste dye will require 12 lbs of barium chloride In all cases where the full deep shade obtainable as barium salt, is required, it is better to use a little more than this proportion, rather than less. Any deficiency of precipitant, such as might be occasioned by the presence of sulphates or carbonates in the dry dye or the dye paste (resulting in precipitation of some of the calculated barium chloride), may yield a lake which is imperfectly converted into the barium compound In the case of Lithol Red, Lake Red P. and Lake Red D , this will cause slight bleeding in oil and solvents generally.

When using calcium acetate or chloride as the precipitant for this class of dyes, a slight but definite excess must be employed, a large excess however must be carefully avoided, as any such excess tends to be adsorbed by the lake particles and is very difficult to remove by mere washing. It is imperative to remove all traces of soluble calcium compounds from the lake before pressing and drying the product, otherwise the dry lakes will be distinctly hygroscopic and almost impossible to keep in a proper dry state during and after grinding If an excessive amount of calcium precipitant has been avoided, and the washing of the lakes is carried out properly by thoroughly stirring the batch of colour (say for 15 minutes) after each filling up with fresh wash water, there should be little risk of producing calcium lakes which become moist on keeping

Each separate dye of this type used must be precipitated under standard conditions to suit the individual dyestuff The bulk of water used should not vary, and the concentration and temperature, as well as the rate of addition of the precipitant, should be standardised to the proved best working formula for each pigment. It will be found best, usually, to add the precipitant when the batch is at a temperature of 80° C and then raise to the boiling point.

In the case of Lake Red C , the precipitation is best effected at 60° C and the subsequent heating should not be continued after the batch reaches a temperature of 98° C.

Lake Red P. is best precipitated at 25° C., then stirred for one to two hours and the temperature finally raised to 40° C The heating should not be carried beyond 40° C , as a much bluer undertone is thus secured. An alternative method to precipitation by means of barium chloride, is to prepare finely divided barium carbonate in suspension in water, using one and a half to twice the weight of barium chloride normally taken for the simple precipitation

This barium carbonate is washed by decantation and added to a warm suspension of the Lake Red P in water (25° C.). The mixture is stirred for 6 hours, allowed to stand overnight and then thoroughly washed. It is pressed and dried in the usual manner This method gives a pale, bright pigment superior in brilliance to that obtained by precipitation with barium chloride

Lithol Red (Monolite Red R)

On account of its great tinctorial power, brightness of shade, its clean bluish undertone and very low price, Lithol Red is still used in far greater quantities than any other pigment red It is only of moderate fastness to light, being just about equal to Lake Red C and in a classification of light fastness ranging from 1 (absolutely fast) to 10 (quite fugitive) it occupies the position 5 In comparison, Permanent red 4B might be taken as 1, Pigment scarlet 3B 1 to 2, Helio red R L 2 to 3, Ponceau 2R. 7, and Ponceau 2G 6

All these are carefully prepared barium lakes except the Permanent red 4B , which is calcium lake, and Helio red R.L which is a pigment dyestuff and not a metallic lake

The preparation of lakes from Lithol red, presents no special difficulties The main considerations are the making or purchase of a standard uniform dye paste with the correct particle size and form Taking a 20 per cent dye paste for purposes of comparison, a dye paste of a thin mobile character, with a greenish-bronze appearance, of a granular or decidedly crystalline form, will not give the best and strongest lakes The paste, at 20 per cent strength which gives the purest shade of lake and of the greatest tinctorial power, usually has a non-mobile form almost like that of a custard This is obviously due to extremely well dispersed particles. Under the microscope at 600 diameters such a paste shows great uniformity of particles, all being very small and in the form of fine needle-like crystals The paste also has a fine rosy-bronze appearance, with a peculiar opaque, or whitish " bloom " when viewed in some lights Once the peculiar characteristic form is known, it can be easily recognised and this will form an excellent preliminary guide to quality A 20 per cent paste which is too heavily bronzed or too fluid at this strength of dry content, will usually give far less tinctorial power owing to the too coarse and refractory crystalline formation, which does not permit of such complete conversion into a well dispersed barium salt.

In making the lake it is best to use a fairly *large* bulk of water with a moderate excess of barium chloride, and to render the water *very faintly* acid with acetic acid before adding the dye paste. The dye paste as bought should be almost free from saline matter and as nearly as possible neutral Actually Lithol red paste will generally show faint alkalinity to the very sensitive type of glazed litmus papers.

The following method will give a good standard product, of full blue undertone and pale bright overtone, with the maximum of tinctorial strength .—

25 Per Cent Lithol Red Lake, on Blanc Fixe

(Batch for a 1,200 gallon vat, *preferably lead lined*)

Steam up 750 gallons water in the vat to 70° C , shut off the steam, then add 2 lbs. 80 per cent acetic acid At this point the stirrer is started and then the Lithol red paste is added before the addition of the base, viz.—4 cwts of 20 per cent paste (or 3 cwts 22 lbs of 25 per cent) The stirring is continued for 10 to 15 minutes in order to disperse the Lithol red fully The base is next added, viz —300 lbs of blanc fixe This is followed by the dispersing agent which may be any one of the following three.

(*a*) 2 to 3 lbs Turkey red oil 50%
(*b*) 1½ ,, 2 ,, Sunlight soap dissolved in hot water
or—
(*c*) 1 ,, 1½ ,, casein dissolved in 1 gallon of water with ¼ pint 880 ammonia

Whichever of these is used, it should be added as a thin fluid

The Sunlight soap gives the finest undertone of the three in many cases, but actual experiment will determine which is the best to adopt for a given result

The batch is now steamed up to 80° C.,stirring continuously, and at 80° C., the barium chloride is added, viz .

Barium chloride	.. . .	100 lbs
	dissolved in—	
Water	.	100 gallons

The batch is stirred constantly and steamed up until a thermometer shows the temperature to be at 98°—100° C Boiling is continued for 10 minutes and finally the vat is filled up with cold water (its finished bulk before filling up, being about 950—1,000 gallons) To ensure the greatest fastness to light the lake must be thoroughly washed. The yield is approximately 4 cwts of finished colour With calcium chloride as precipitant, Lithol red yields a crimson-maroon shade of lake which is slightly faster to light than the barium salt. The pure calcium salt of Lithol red, which is doubtless prepared by using a calcium compound of one or both of the dye constituents, has been marketed under the name of Lithol Red 3B., as an insoluble pigment dye.

The general rules governing the production of pigments or lakes from soluble and slightly soluble acid azo dyes are given below —

1. The content of soluble sulphates and carbonates in the dyestuff, whether in paste or powder form, will materially affect the shade of the finished lake. These substances should only be present to a minute degree, and whatever proportion is present, this should be known and allowed for in calculating the amount of the precipitant.

2. A distinct excess of precipitant should always be used, the excess being completely eliminated from the finished product by thorough washing.

3 The content of all soluble salts, other than any needed for special effects in the precipitation (see Pigment scarlet 3B. p 166), should be as low as possible in both dye powders and pigment dye pastes

4 The most favourable physical conditions for every phase of the operations must be carefully noted and, once determined, should be rigidly adhered to even for the simplest types of pigments.

5. Lakes should be prepared by making small laboratory trials of every batch or delivery of dyestuff, before using it on a works scale, in order to compare its purity and uniformity with previous standards. Any variations or faults in the dyestuff may then be allowed for or corrected if possible in the works scale operation. Where any such rectification is neither advisable nor practicable, the dyestuff should be rejected, rather than produce a large batch which is not of standard shade and quality.

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CHAPTER XXII

"REFLEX" LAKES

THE Permanent red lakes, described on pages 212 to 214, when used in the form of pure metallic salts, form the basis of the most useful scarlet to Bordeaux shade lakes for obtaining heavily bronzed effects in printing

Other dyestuffs suitable for this purpose are—

	Shade of Lake
Acid Eosin (Bromofluorescein)	
As Barium salt. Moderate fastness to light	Pale rosy-scarlet
As Lead salt	Deep scarlet with intense greenish-golden bronze.
Lake Red P. (*I. C. I*)	
As Barium salt. Fairly good fastness to light	Slightly deeper and duller than above. Bronze effect not very pronounced.
Monolite Red R. (*I. C. I*) (Lithol red) (Alliance Co., Ltd.)	
As pure Barium salt. Moderate fastness to light	Pure bronzy-red shade.
Permanent Red 4B. (*Major & Co*) (*I C. I.*)	
As pure Calcium salt or mixed Calcium and Strontium salt. Very fast to light	Pure deep red shade. Good bronzing.
Permanent Red B. (*Major & Co.*) (*I C I.*)	
As pure Calcium salt or mixed Calcium and Strontium salt Very fast to light	Pure scarlet shade, very blue undertone.
Helio Red R M.T. (*I.G*)	
As Lead salt. Moderate fastness to light	Pure rosy-scarlet shade.
Lake Fast Rubine B.L (*Leitch & Co.*)	
Very fast to light	Pure scarlet shade.
Permanent Red F4.R.H (*I G*)	
Very fast to light	Pure bright crimson shade.
Helio Bordeaux B.L (*I G*)	
Calcium salt Good fastness to light	Deep dull crimson shade

Other Shades.—Apart from various shades of bronzing Prussian blues, the following are used for reflex blues and violets :

Methyl violet (as pure Barium salt)
Acid violet („ „ „ „)
Acid magenta („ „ „ „)
Alkali blue („ „ „ „).

Hæmatine crystals or logwood extracts are used for bronzing blacks (see page 242). Other bronzing blacks are produced from free acids of sulphonated Nigrosines, such as Blue black E.V. (Kalle) Irisin black K G (A.G.F.A.).

The Fanal colours, of which a list is given on p 205, when in their pure state, as tungstomolybdates, form a series of exceptionally strong bright "reflex" lakes, rather high in price, but correspondingly strong, bright, and fast to light.

Essential features for the production of reflex lakes are—

1. Entire absence of any substratum or other substance which might modify the physical form of the metallic salt, or give rise to milkiness. Therefore in all such processes extreme care and cleanliness are necessary, and the lakes must not be contaminated at any stage.

2. As the special appearance is due to a particular physical form, *viz. microcrystalline structure*, the whole process must be rigidly controlled, i.e. dilution of each component, temperature, rate of stirring, rate of precipitation, amount and strength of Turkey red oil, and finally *the method of grinding*.

3. Eliminating any accidental precipitation of lead, barium or calcium sulphate, or carbonate, or other opaque or milky impurity, as the least trace of any such foreign substance greatly impairs the bronzing No water with a high natural saline content should be used for making these colours Another precaution that may well be taken is to make sure that dye pastes or powders to be converted into " reflex " lakes, do not contain soluble sulphates or carbonates, for these on conversion of the dye into the latter would produce lead, barium or calcium compounds which would have the effect above mentioned.

4. Obviously no substratum, even if quite transparent, should be used in making these " Lakes " or dye-salts as they might more properly be termed.

Two typical examples are given below:—

REFLEX BLUE

Reflex Blue

14 lbs.	"Alkali blue for reflex blue" dye

are dissolved in—

40 gallons	Water at 150° F.

to which have been added—

3 lbs.	Turkey red oil (50%)

The solution is brought to the boil, and at 212° F. is precipitated with—

25 lbs.	Sulphuric acid

It is next boiled for 1 hour and then—

5 lbs.	Sugar of lead in—
5 gallons	Water

is added while stirring at 210° F.

Finally *unwashed* alumina paste made separately from—

12 lbs.	Aluminium sulphate
6 ,,	Soda ash.

is added.

The batch is now diluted with 45 gallons of cold water and allowed to stand overnight. Next day it is syphoned off and the colour paste pressed hard in a screw-press (see Fig. 22. p. 38).

The press cakes (which must not contain above 50 per cent water), are beaten up *until quite uniformly smooth* in a paste mixing machine (Werner-Pfleiderer), and then to the wet paste is added 14 lbs. of medium stout lithographic varnish.

The mixture emulsifies, but after a time the water separates out, leaving a paste *in oil from which the final traces of water separate* on grinding on the roller mill. This particular colour cannot be successfully made as a dry powder and therefore is usually made up direct as described The paste as above made is further diluted with litho varnish as required before use.

Reflex Lake Red C —The pure barium salt of Lake red C. if properly made is of very soft texture and pure rosy-red undertone. The overtone is not heavily bronzed in appearance, but has a pure golden sheen

To make the reflex lake successfully it is essential to work at the proper dilution and to precipitate at the correct temperature, finishing the conversion at 212° F. by steam boiling for 10 minutes.

Other important points are—

(1.) The dye paste of Lake red C. should be in the correct form, i.e. a thin gelatinous paste of pale clean orange-scarlet shade, with a distinctly milky or opaque sheen.

(2.) No excess of Turkey red oil is permissible, as with excess a heavier shade is produced and a hard, brittle dry colour results.

(3.) As used, the paste must be free from alkali and is best when faintly acid with acetic acid.

An alkaline reaction of the paste dye mentioned in (1) gives the same hard, brittle oven product on drying. The paste dye usually contains about ½ to 1 per cent of Turkey red oil on the total paste weight. If any Turkey red oil has to be added in the process, not more than this amount is permissible. When these points are carefully observed the process is simple.

Working details: 2 cwts. of 20 per cent Lake red C. paste are well stirred in 150 gallons of warm water, (100° F) and, if necessary, the mixture made very faintly acid to glazed litmus paper by adding 2 per cent acetic acid cautiously. Steam is then turned on and the batch stirred. At 160° F. the barium chloride is added rapidly, with good stirring—50 lbs. barium chloride in 40 gallons water at 160° F The heating and stirring are continued until the temperature is at 210° F. Steam is then shut off and 50 gallons cold water run in The lake is well washed by decantation and dried at 200° F. This lake has very good heat resisting properties, being far superior, for example, to Lithol red and Pigment scarlet 3B.

Acid Eosin Reflex Lake.—When it is desired to produce a bright red lake with very pronounced golden bronze sheen, Acid Eosin gives this effect to the fullest degree. The dye is precipitated as a pure lead salt, and in this dense form is of reasonable fastness to light.

As this particular dye gives a bronzing lake with a fine metallic sheen, scarcely equalled by any other known type, it is of considerable value in spite of its only moderate fastness to light.

CHAPTER XXIII

Alizarin and Madder Lakes

THE writer is much indebted to the British Alizarine Company Limited for their courtesy in placing freely at his disposal the results of the extensive experiments which have been carried out in their laboratories on the manufacture and properties of Alizarin Lakes

Alizarin is remarkable for the great variety of shades obtainable from it by merely altering the proportions of reagents and the method of precipitation. It is therefore necessary to give a much greater number of typical processes in order to describe the possibilities of the dyestuff adequately.

The natural colouring matter is extracted from the root of the madder plant which is a member of the order Rubiaciæ, indigenous to various countries in Asia and Southern Europe. It has been known for many centuries as a brilliant fast dye, giving lakes of scarlet, carmine, and purple shades. With the introduction of large scale cultivation of the plant in India and Turkey, and a more scientific investigation of its use and properties, varied shades were more regularly and accurately obtained from this natural dyestuff. According to the method of treatment of the roots for the extraction of the colouring matter it is possible to obtain :—

(*a*) Alizarin itself 1 2-dihydroxyanthraquinone.
(*b*) Purpurin, 1 : 2 : 4-tri-hydroxy anthraquinone
(*c*) Other subsidiary anthraquinone derivatives.

As the colour producing pastes obtained from the natural roots varied slightly in composition and in the percentage of glucosides or other vegetable "impurities," only highly skilled workers could obtain the best results, and uniformity of shade and other properties could only be attained by long experience.

Natural madder is still used in France on a small scale for the production of fine artists' colours, and these are said to be very bright. However it is often the case that a brilliant-looking Alizarin lake proves to be considerably less bright when ground in oil than many apparently duller kinds.

The actual working processes for the production of these natural madder-root lakes are almost in the nature of an hereditary business and are therefore not within the scope of this book.

Alizarin was first isolated from madder roots by Robiquet and Colin in 1826[*], and was first made synthetically from anthraquinone by Græbe and Liebermann in 1868[†].

The synthetic alizarins cover a much wider range of shades than can be obtained from the natural product, and yield lakes of the same properties and fastness. In addition the synthetic product offers the advantages of absolute uniformity of chemical composition

The following is a list of the principal shades manufactured by the British Alizarine Co , Ltd. :—

Red Shades :
  Alizarin 3 P., 20% (extreme blue shade).
  Alizarin 2.P., 20%.
  Alizarin I.P., 20%.
  Alizarin S X., 20%.
  Alizarin S S.A., 20%
  Alizarin Y.C A., 20%
  Alizarin C A.F., 20% (extreme yellow shade).

Violet and Bordeaux Shades .
  Anthracene blue B.A., 10%.
  Alizarin cyanine A.C , 20%.
  Alizarin Bordeaux B.A , 20%.
  Alizarin Bordeaux B A R., 20%.
  Brilliant alizarin Bordeaux R , 17%.
  Alizarin Bordeaux B.A.Y., 20%
  Alizarin maroon, 20%.

Orange Shade .
  Alizarin orange, 20%

Blue Shade
  Alizarin blue S powder.

Brown Shade
  Anthracene brown G , 20%

The alizarins belong to the " mordant dyestuff " class, and they owe this property to the presence of two hydroxyl groups in the 1 : 2 positions of the anthraquinone molecule.

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[*] Polytechnic Journal 27, 549.
[†] Bericht 2, 223, 3, 634.

These are capable of forming with aluminium and calcium a very complex inner salt which is of great stability Although many theories have been advanced as to the composition of Alizarin lakes, the subject is still a matter of controversy.

Liechti and Suida give the formula as Al_2O_3 CaO $(C_{14}H_6O_2)3$ H_2O Apart from aluminium and calcium, Turkey red oil appears to perform a more than purely physical function and to enter into actual chemical combination with the alizarin

In addition to aluminium, such metals as chromium, iron, nickel and tin form similar combinations, although these are of less interest to the lake maker

Although the methods for the preparation of Alizarin lakes vary greatly in detail, the combination is always brought about by boiling the Alizarin with aluminium hydroxide in the presence of Turkey red oil, and a salt of calcium ; the suspension is neutral or slightly acid. Phosphates of aluminium or calcium are usually incorporated and these considerably improve the resulting lakes.

In fitting up a plant for the manufacture of Alizarin lakes, great care should be taken that efficient boiling can be obtained.

The usual plant consists of a wooden vat, preferably fitted with a mechanical stirrer, the heating being effected by means of a closed copper steam coil

While a higher temperature is obtained, as described above, very good lakes can be obtained by passing the steam directly into the precipitation mixture by means of a perforated lead coil. When using such a system, great care must be taken to avoid accidental contamination with rust or metallic iron from the main steam pipe lines One form of safeguard is to introduce a steam reservoir of ample size made of copper, or else lead-lined, between the main steam line and the lead branch pipe to the vat. Any " rusty " water or solid particles will be retained in this catch pot, which may be drained periodically by means of a tap in the base

Two or more run-off pipes should be fitted to the vat, one on the bottom, the others being in a suitable position on the side of the vat for the purpose of removing the clear liquor when washing by decantation

The brightest lakes are obtained by heating under pressure in a copper or lead-lined autoclave at a pressure of 3 to 5 atmospheres, but the cost of the plant is scarcely worth the small improvement in brightness obtained.

In view of the great sensitiveness of Alizarin towards iron, all iron nails and pipes should be carefully excluded, and, when using compressed air as an auxiliary means of agitation, iron rust from the inside of pipes should be scrupulously guarded against This can be done by including a trap in the system (see above). The water supply should also be periodically tested

A trace of iron in an Alizarin red lake gives a flat blue undertone, and a dark brownish overtone when the pigment is rubbed out in oil.

Iron, when used in place of aluminium as a constituent of the lake, gives a violet pigment of great strength, but dull and heavy in shade. This lake, and those produced with a mixture of iron and alumina, have definite uses where fastness is of paramount importance, but they are gradually being replaced by the lakes obtained from brands of Alizarin Bordeaux, which are much brighter in tone

The choice of a method depends upon the shade and properties required. Nearly every colour works has its own closely guarded recipes, giving widely different results. A remarkable property of Alizarin is the number of different tones obtainable from the same brand of dyestuff by altering the quantities of the reagents or the method of precipitation

The methods given below are typical

METHOD A.

This method can be used for all paste Alizarin dyestuffs.

1. Aluminium sulphate (18—19% Al_2O_3) 33 5 parts in 335 parts water.
2 Soda ash . 17 1 parts in 171 parts water.
Precipitate at the boil, boil for 1 hour, filter or wash several times by decantation
Make up to 800 parts, and add the following in the order given :
3 Sodium phosphate . 8 2 parts in 82 parts water.
4 Calcium chloride : 14.5 parts in 145 parts water.
5 Turkey red oil (50%) : 13 0 parts in 130 parts water
6 Alizarin paste (20%) · 40.0 parts in 224 parts water.
Stir continuously during the addition. Bring up to the boil slowly, during 2—3 hours Boil for 5 hours Filter and wash.

The dry lakes obtained by this method are bright in appearance and soft in texture Ground in oil they are moderately transparent.

To obtain strong lakes with the red shades of Alizarin, up to 60 parts of colour paste may be used in the above recipe.

As the ratio of Alizarin to aluminium hydroxide is increased, the lakes become lighter in overtone and bluer in undertone The same result can be brought about to a certain extent by the addition of a little acetic acid to the precipitation mixture before adding the Alizarin.

Maroon shades can be obtained from Alizarin 1P. by the addition of salts of iron, nickel, or chromium.

Method B

This method gives much more transparent lakes than those produced by Method A. They have a slightly lower oil absorption, and do not possess the same brightness when dry, but they give beautiful tones in oil.

The method can be used with all Alizarin dyestuffs in paste form, excepting Alizarin Orange and Anthracene Brown, which give dull lakes when precipitated from an alkaline solution, and the method must be modified as described below.

The chemicals are added in the following order and the precipitation is carried out in the cold :

1 Sodium phosphate · 47 parts in 940 parts water
2 Alizarin, 20% paste : 66 parts in 660 parts water.
3 Soda ash : 18 parts in 180 parts water.
4 Turkey red oil (50%) : 19 parts in 190 parts water.
5. Aluminium sulphate (17—18% Al_2O_3) · 56 parts in 560 parts water.
6. Calcium chloride (flakes) . 9 parts in 90 parts water

The aluminium sulphate must be added very slowly Bring to the boil in 3 hours and boil for 3 hours. Filter and wash.

Alizarin Orange and Anthracene Brown

This method can be modified for use with Alizarin Orange and Anthracene Brown in the following way. The same quantities and dilutions can be used, but the chemicals in the above list are mixed in the following order—

2, 5, 1, 3, 4, 6

It is best to mix 1, 3 and 4 together in a separate vat before adding

Method C.

This gives lakes similar in characteristics to those produced by Method B, but of lower concentration It is particularly suitable for use with shades of Alizarin Bordeaux. The chemicals are added in the following order :—

1 Sodium phosphate . 21 parts in 600 parts water.
2. Alizarin Bordeaux (20%) : 12 parts in 48 parts water.
3. Soda ash · 5 parts in 50 parts water.
4. Turkey red oil (50%) · 5 parts in 50 parts water.
5. Aluminium sulphate (17—18% Al_2O_3) 22 parts in 220 parts water.
6. Calcium chloride (flakes) · 1.5 parts in 15 parts water.
Bring to the boil in 3 hours and boil for 3 hours. Filter and wash.

Method D.

This method is used for producing red shades of blue with Alizarin Blue S.

1. Aluminium sulphate (17—18% Al_2O_3) : 33.5 parts in 355 parts water.
2. Soda ash · 17 1 parts in 171 parts water
Precipitate hot, boil for 1 hour, filter or wash several times by decantation Make up to 600 parts and add the following in the order given
3 Sodium phosphate : 8 2 parts in 82 parts water.
4 Calcium chloride : 14.5 parts in 145 parts water.
5 Turkey red oil : 13 0 parts in 130 parts water.
6. Alizarin Blue S. powder : 17.5 parts in 300 parts water.
Allow to stand, after stirring well, preferably overnight Bring to the boil in 2 to 3 hours, boil for 3 hours, and filter warm.

Method E.

This method is used for producing green shades of blue with Alizarin Blue S.

1. Aluminium sulphate (18% Al_2O_3) 20 parts
2 Nickel sulphate : 7 parts.
3. Soda ash · 13 parts
4. Sodium phosphate · 4 95 parts
5 Calcium chloride . 8.7 parts
6 Turkey red oil (50%) . 7 8 parts
7. Alizarin Blue S powder . 12 8 parts.
Method and dilutions as in D

Method for Cheap Alizarin Red Lakes
for
Paint and Distemper Manufacture

The chemicals are added in the order given :

1. Alizarin, 20% : 97 parts in 1,000 parts water
2. Alum (ammonia) . 28.6 parts in 286 parts water.
3. Blanc fixe 50 parts made into a thin paste.
4 Turkey red oil (50%) : 20 parts in 200 parts
5. Lime · 4 parts slaked overnight and added cold with continuous stirring
Bring the mixture to the boil in 2—3 hours, and add—
6 Lime : 3 parts slaked and added hot.
Boil the whole for 3—4 hours, filter and wash.

Note.—The slaked lime is added through a sieve

Method for Chromium Lakes

The chemicals are added in the order given :—

1. Alizarin, 20% 50 parts in 750 parts water.
2. Blanc fixe : 60% parts made into a thin paste.
3. Turkey red oil (50%) 15 parts in 150 parts water,
4. Chromium acetate solution (15% $K_2Cr_2O_4$) : 48 parts in 500 parts water.
5. Lime 4 7 parts slaked and made up to 500 parts.
   Bring to the boil in 2 to 3 hours. Boil for 3 hours. Filter and wash.

The above method gives the following shades :—

Alizarin 1P.	Maroon.
Alizarin Orange	Light red-brown.
Alizarin Bordeaux B A.	Violet.
Alizarin Blue S	Blue.
Anthracene Brown	Brown.

Owing to the number of different lakes obtainable from one brand of dyestuff, the problem of matching an Alizarin lake is a very difficult one. The only method is to make small scale experiments, carried out under the same conditions, and with water and chemicals from the same sources as those which will be used in the actual works process Alizarin is so sensitive to the slightest variation in the conditions of manufacture that a recipe cannot be passed from one works to another with any certainty of the exact lake being obtained.

If it is doubtful what brand of Alizarin has been used in making the lake to be matched, the following tests can be quickly carried out

A small portion is decomposed by heating with pure concentrated hydrochloric acid and, after dilution, the yellow precipitate is filtered off and washed.

The precipitate is dissolved in an excess of potassium carbonate solution and compared in tubes with similar solutions made up from standard brands of Alizarin. The solutions must be dilute, of equal depth, and contain relatively about the same excess of potassium carbonate.

The variation shown by different brands of Alizarin is very marked and after a little practice the brand used in a lake can be quickly recognised.

The acid filtrate is tested for phosphates by the molybdate method and for aluminium, iron, and other metals, if such be suspected.

CHAPTER XXIV

Lakes from Natural Dyestuffs : Appendix Lists of Dyestuffs

Colours from Natural Dyestuffs

This range is chiefly made up of colours from

Madder Root extract (almost obsolete owing to the great uniformity and wider range of the products from its synthetic counterpart Alizarin) see pages 231 to 237.

Cochineal Insects, produced from the dyestuff contained in the female of a beetle (*Coccus Cacti L.*) found on various cactus plants, chiefly in Mexico, but also in Australia, Algeria, and other countries. The lakes from this dye are not in general use owing to variations in properties and difficulties in manufacture, but they have a distinct use because of their great fastness to light, and rich bright tones obtainable.

Lima Wood Various lakes of claret red to Bordeaux shades are known as rose pink These when properly made have good fastness to light and are reasonable in price. They are still widely used as opaque undercoatings for expensive crimson and maroon lakes of a more transparent nature.

Persian Berries and Quercitron Bark Pigments made from these are generally known as "Dutch Pinks" They are transparent lakes, which in oil have a deep khaki overtone and a rich greenish-yellow undertone. Pure bright shades of these lakes are invaluable for obtaining deep rich shades of green and brown by incorporating with them Chrome greens or siennas, umbers, blacks, etc , as the case may be. The best and richest shades are made from Persian berries, the price of which, however, makes their use prohibitive to-day, except for fine artists' colours.

Other wood extracts used are those from—Peach wood, Red wood, Logwood, etc., which are still used in calico printing with various mordants for obtaining cheap and very fast to light shades. They are not used in lake making to-day with the exception of Logwood which as a purified product, Hæmatin crystals, is sometimes used for black bronzing lakes for printing inks

Ligneous Deposits. Some partly fossilised wood or root deposits contain appreciable quantities of a brown dye substance. The pigment colour manufactured from such sources is known as Vandyke brown, and is very useful and widely employed for making rich deep browns for coach and motor painting, etc The best product is obtained by suitable treatment of well-aged deposits of peat, or partly carbonised heather-roots. Similar products have been obtained by the same method of procedure with partly "baked" sawdust, or with leather cuttings and dust.

Madder. It has been often claimed that natural madder lakes were of superior brilliance to those made from Alizarin. To-day this is certainly not the case, because of the purity and wide range of Alizarin products. Therefore owing to the high skill required, and the impossibility of guaranteeing really uniform results when making lakes from madder root extract, they have been almost entirely superseded by the corresponding Alizarin lakes which are of equal brilliance, and more consistent in general properties and fastness to light. No useful purpose is therefore served by attempting to give working details for natural madder lakes

Cochineal. The cochineal lakes have an extremely deep rich tone and yield brilliant dark crimson to plum-coloured lakes, with vivid bluish undertone, and very fast to light These characteristics give them a certain definite utility, for although they are high in price and are only made successfully by very few manufacturers, there are no synthetic dye lakes which quite take their place There are not more than one or two firms in England and three or four in France who still make satisfactory cochineal lakes The processes are very roundabout and complicated, numerous ingredients being used apparently without any definite logical explanation, but all apparently essential The author has seen cochineal lakes made in which all the following ingredients were used—cochineal insects, fine glue, borax, starch, alumina, alum, cream of tartar, Turkey red oil and tin crystals The lake maker was quite convinced that all these were really essential and possibly they were, but on the other hand, even if one or more not really essential had been left out, doubtless the psychological effect on the lake maker would have been as disastrous as omitting an essential ingredient. In making cochineal lakes, by whatever method, the greatest care has to be taken to exclude rigorously any possibility of contamination with iron, otherwise the colour is most easily rendered dark and full. The chief precipitant or lake-forming metal used is tin, although some aluminium and some calcium enters into the composition of many of the lakes

Cochineal lakes are sometimes prepared from " Ammoniacal Cochineal Liquor," made by digesting the insects with water and ammonia, filtering and evaporating the excess ammonia.

No attempt can be made to give formulæ for these lakes with any guarantee that they will give perfect results, as long experience and practice are essential Two working methods are given below which form a general guide to the procedure and will give quite good results if carefully worked .—

Pure Cochineal Carmine

Ingredients .

14 lbs.	Gelatin (Coignets Gold Medal)
10 ,,	Citric acid pure crystalline
150 ,,	Ground cochineal insects
28 ,,	Borax.
18 ,,	Powdered alum.

(*a*) Soak the gelatin overnight in 30 gallons cold water.

(*b*) Prepare a boiling solution of the citric acid in 30 gallons water. Add (*c*) to this

(*c*) 150 lbs. dry ground up cochineal.

(*d*) Boil (*b*) after adding (*c*) for 20 minutes. Add (*a*) melted up by heating to 80° – 90° C.

(*e*) Boil the three mixed ingredients for a further ½-hour, boiling vigorously. *Allow to cool to* 60° *C.* Next strain through a fine sieve (made *entirely* of copper) and then through very fine flannel or muslin cloth into the striking vat. Boil up this clear solution and remove all scum that forms, with a fine copper gauze sieve or screen

(*f*) Slowly add the borax in powder form while boiling the clear bright solution.

(*g*) Boil a further 10 minutes, then add the alum, dissolved in 10 gallons water, and boil for a further 1 to 1½ hours

After cooling and standing for 1 day, the top liquor is slowly syphoned off and the remaining colour is filtered, and then *must be rapidly dried at a low temperature* This is to avoid decomposition and the formation of mildew, owing to the large content of easily attacked gummy and albuminoid compounds contained in the lake. The usual procedure is to " knock " the paste colour into small conical drops, through a flat bottomed (copper) colander bored with ½ inch to ¾ inch holes, on to the drying trays Glass trays should be used, and a good current of air maintained in the oven. Sound, clean, oaken vats should be employed and should not be used for any other process Any metal utensils used must be in pure copper, but glazed earthenware is even preferable when possible to use it.

All boiling up must be done with a closed copper steam coil, open steam boiling is out of the question and of course nothing but copper fittings may be used in the vat.

All salts and ingredients must be of pure, iron-free quality

COCHINEAL CRIMSON

Ingredients

30	lbs.	Ammonium Carbonate.
84	,,	Potash alum (iron-free quality)
28	,,	Potassium carbonate (iron-free quality).
2	,,	Sulphuric acid (iron-free quality)
10	,,	Potash alum (iron-free quality).
38	,,	Cream of tartar (iron-free quality)
2	galls	New milk.
1	cwt.	Cochineal (ground-up powder)
10	,,	Tin crystals.

Procedure :

(*a*) *White base.*
Dissolve the ammonium carbonate in 80 gallons of water at 40° C. To this solution add a boiling solution of the potash alum (84 lbs.) in 40 gallons water, with fast stirring meanwhile. Conduct this operation in a vat of at least 600 gallons capacity. When the frothing has subsided, stir for 10 minutes and fill up to 600 gallons. Wash thoroughly and settle to about 100 gallons bulk

(*b*) Boil up 70 gallons water with the 2 lbs. sulphuric acid, add the powdered cochineal and boil 15 minutes, then add a boiling solution of the 28 lbs. potassium carbonate in 15 gallons water

(*c*) Boil for 15 minutes longer, then add the 10 lbs. potash alum as a concentrated solution Stir for another 5 minutes, and then strain the liquid quite clear

(*d*) Allow the liquor to stand 3 to 4 hours. When cooled to 50° C. *slowly* sift in the dry cream of tartar, stirring all the time the addition is made.

(*e*) Stir 10 minutes, and then add the tin salts over a period of 10 minutes.

(*f*) Then add 2 gallons of new milk and allow the liquid to stand 12 hours. The next day run in the white base (*a*) which is ready washed and prepared. Wash once by decantation, filter to hard cakes and dry rapidly.

ROSE PINK

The finest lake product is made from the dye wood known as Lima wood, which is a wood of similar variety to Campeachy wood or Logwood (see below)

Lima wood is chiefly obtained from Brazil and Mexico, and is also known as Brazil wood, Pernambuco wood, etc. Most of this wood, of which there is a limited output is bought by dye-wood extracting firms, who use high temperature methods quite suitable for dye wood extracts for textile work, but not for the production of the brightest and most useful lakes. For this reason the lower grades of rose pink tend to remain at a low price, while the stronger brighter shades become increasingly expensive No working method need be given for these lakes. They are prepared from the dye liquor on a whiting base with aluminium sulphate, and therefore the lakes contain calcium carbonate and sulphate

LOGWOOD BLACKS

Various extracts of Logwood are made and used chiefly in wool dyeing. The most concentrated and purified form being in crystal form and sold as " Hæmatin crystals."

When the better varieties of fluid Logwood extract are precipitated on to a completely transparent base, such as *starch*, with tin as a precipitant, the resultant lake has a fine bronzy black appearance (see " reflex " lakes, p. 229) Precipitated on to mixed alumina, blanc fixe or *on to iron hydrate base*, by means of chromium and iron salts, the lakes have a greenish-black to bluish-black appearance and are used where a true black tone is required, without great covering power A well-prepared lake of this type, when tested in oil, makes a good Vine black appear to be of a distinct grey tone in comparison

" DUTCH PINK "

The remarks concerning dye-extracts in the paragraphs dealing with rose pink, also apply to this colour (the dyestuff of which is of the " Flavonol " class) The general method of precipitation is the same, and all the ordinary lake qualities at least contain calcium carbonate and/or sulphate as a base

No other special details can be given as the market for this type of dye-wood colour is limited and its manufacture is almost a monopoly in England.

VANDYKE BROWN

The best grades of this are prepared from good, clean peat deposits, which have been well " carbonised " by slow formation and long weathering. Suitable deposits can only be found by trial of likely looking " beds."

The material has to be dug out as free from earthy and other impurities as possible, and should be *non-fibrous* and deep brown, almost black in colour when wetted The method of extraction is to macerate the ground-up peat with hot water and caustic soda Sufficient caustic soda must be used to produce a definite alkalinity, but no more This point cannot be determined by test paper, so is usually determined by the rule-of-thumb (although remarkably accurate) method of testing the liquor for the first definite " soapy " feel between finger and thumb, while adding the caustic soda. A more certain method is to add a few ounces of ammonium chloride to the macerated peat when adding the caustic soda; *immediately* the least free alkalinity appears, the liquor has a distinct smell of ammonia. No definite proportions of caustic soda nor yields of colour can be given, as they vary enormously with different peat deposits.

The liquor prepared as above is well boiled and strained, then concentrated by evaporation and dried, usually with some dextrin added, to form a solid substance known as " Vandyke crystals " This is practically all soluble dyestuff, but contains usually some cloudy matter in the form of vegetable and carbonaceous impurities. It is used as a wood stain, and for staining leather, paper, confectionery, etc. The crystals, or better the liquor before drying off, is used for the precipitation of Vandyke brown pigment, of the better qualities, and the still purer pigment known as Bistre

Cheaper brown pigments of the same type are made from more earthy deposits of partly fossilised peat, or of lignite or brown coal, such as are found in Germany These pigments are made by simply washing and grinding the material as dug or mined, without soda extraction.

Such a type is much used on the continent under the name of " Cassel Brown "

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APPENDIX I

BOOKS AND ARTICLES OF GENERAL INTEREST

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(13) " Kunstliche Organische Pigment Farben " C. A. Curtis. (Verlag von Julius Springer, Berlin, 1929.)

(14) " Pyroxylin Enamels and Lacquers " S. P. Wilson. (Constable and Co., Ltd., 1928.)

(15) " Colours for Cellulose Lacquers " H A. Nelson and W C Norris. (Paint, Oil and Chem. Rev., 1927, 84, 10.)

(16) " Outline of Paint Technology " Noël Heaton. (Griffin and Co , Ltd , 1928)

(17) " Die Neueren Farbstoffe der Pigmentfarben—Industrie." R. Staeble. (Julius Springer, Berlin, 1910.)

APPENDIX II

LISTS OF DYESTUFFS FOR LAKE MANUFACTURE

PAGE

(1) *Alliance Colour and Chemical Co, Ltd* 247
(2) *Imperial Chemical Industries, Ltd* .. 249
(3) *The Clayton Aniline Co, Ltd.* 256
(4) *Emco Dyestuffs Ltd.* 263
(5) *L. B Holliday & Co, Ltd* 267

THE ALLIANCE COLOUR AND CHEMICAL CO, LTD.

DYESTUFFS FOR LAKE MANUFACTURE

Class	Name	Remarks
Insoluble Azo dyestuffs, with no lake forming properties	(1) Helio Fast red R L paste and lumps	*Shade* —Brilliant scarlet *Uses.*—Fast to light printing ink colours, wallpaper and paper surfacing colours, oil, distemper and water paint colours
	(2) Permanent red R paste and lumps	*Shade* —Red orange or scarlet *Uses* —Fast to light printing ink colours, wallpaper and paper surfacing colours, oil and water paint colours, and linoleum colours
	(3) Permanent red 2G paste and powder	*Shade:*—Orange-red *Uses* —Fast to light printing ink colours Wallpaper and paper surfacing colours, oil and water paint colours, and linoleum colours
	(4) Lithol fast yellow 2G paste and lumps	*Shade*·—Full yellow. *Uses* —Fast to light and lime Principally used for distempers
	(5) Lake green B	*Shade* —Yellowish-green *Uses:*—Wallpaper and paper surfacing colours, distemper and cement colours Fast to light.
Insoluble or partially soluble azo dyestuffs which possess lake forming properties	(1) Lake red C paste	*Shade* —Bright yellowish-red, possessing fine bluish undertone The barium salt gives a rich bronze scarlet. *Uses* —Printing ink colours, linoleum and rubber colours
	(2) Lithol red R paste	*Shade:*—Bright bluish-red as barium lake Bluer shade as calcium lake. *Uses*·—Printing ink colours, oil and water paint colours, and distemper colours

Class	Name	Remarks
Acid dyestuffs	(1) Acid orange	*Shade*—Bright yellowish-orange *Uses* —Printing ink colours, paper surfacing and oil colours
	(2) Brilliant orange O.	*Shade:*—Bright orange *Uses* —Printing ink and paper surfacing colours
	(3) Brilliant orange R	*Shade*—Bright reddish orange. *Uses* —Printing ink and paper surfacing colours.
	(4) Crocein orange	*Shade* —Yellowish-orange. *Uses* —Paper surfacing colours
	(5) Lake scarlet R X.	*Shade* —Bright bluish-scarlet *Uses.*—Printing ink and paper surfacing colours.
	(6) Lake scarlet R C.	*Shade* —Bluer shade than the " R X." brand. *Uses* —Printing ink and paper surfacing colours
	(7) Lake scarlet 2G	*Shade* —Yellowish-scarlet *Uses* —Paper surfacing colour.
	(8) Brilliant scarlet 2G N B paste	*Shade* —Yellowish-scarlet. *Uses* — For lakes fast to bleeding in benzene.
	(9) Pigment scarlet 3B.	*Shade*—Scarlet top tone, good bluish undertone *Uses:*— Fast to light printing ink, and oil colours
	(10) Lake Bordeaux B.	*Shade* —Bluish-Bordeaux shade *Uses* —Printing ink and paper surfacing colours
	(11) Naphthol green B	*Shade* —Yellowish-green of very good light fastness *Uses* —Printing ink colours, wallpaper and paper surfacing colours, and distempers

Class	Name	Remarks
	(12) Nigrosine crystals	*Shade* —Good black. *Uses* — Printing ink and paper surfacing colours
Basic dyestuffs	Chrysoidine R	*Shade* —Yellowish-brown. *Uses* — Printing ink and paper surfacing colours
Miscellaneous	Lake yellow R	*Shade* —Full yellow *Uses* — Wallpaper and paper surfacing colours

IMPERIAL CHEMICAL INDUSTRIES LIMITED

DYESTUFFS FOR LAKE MANUFACTURE

Class	Name	Remarks
Insoluble azo dyestuffs with no lake-forming properties	(1) Monolite fast scarlet R N S paste and lumps	*Shade* —Brilliant scarlet *Uses* — Fast to light printing ink colours, wallpaper and paper surfacing colours, oil and water paint colours, and distemper colours.
	(2) Monolite red 2G S paste	*Shade* —Orange-red *Uses* — Fast to light printing ink colours, wallpaper and paper surfacing colours, oil and water paint colours, and linoleum colours
	(3) Monolite red B S paste and powder	*Shade* —Bluish-red *Uses* — Fast to light wallpaper and paper surfacing colours, distemper colours, and oil and water paint colours
	(4) Monolite fast red G S lumps	*Shade* —Brilliant yellowish shade of red *Uses* — Fast to light oil and water paint colours, printing ink and paper surfacing colours, and wallpaper and linoleum colours

CLASS	NAME	REMARKS.
	(5) Monolite yellow G S paste and powder	*Shade* —Pure greenish-yellow *Uses* — Fast to light printing ink colours, wallpaper and paper surfacing colours, oil and water paint colours, and distemper colours.
	(6) Lake green B S paste, powder and concentrated lumps	*Shade* —Yellowish-green. *Uses.*— Fast to light wallpaper and paper surfacing colours, distemper colours, and cement colours
Insoluble or partially soluble azo dyestuffs which possess lake forming properties.	(1) Monolite red P S paste	*Shade* —Bright yellowish-red. *Uses* —Printing ink colours, and linoleum colours
	(2) Monolite red D S paste	*Shade* —Bright yellowish-red *Uses* — Printing ink colours
	(3) Monolite red C S paste	*Shade* —Bright yellowish-red possessing fine bluish undertone *Uses* —Printing ink colours, linoleum and rubber colours
	(4) Monolite red R S paste and powder	*Shade* —Bright bluish-red as barium lake Bluer shade as calcium lake. *Uses* — Printing ink colours, oil and water paint colours, and distemper colours
	(5) Monolite Rubine B N S paste	*Shade* —Fiery red as barium lake, pure bluish-carmine as calcium lake *Uses* — Printing ink colours, wallpaper and paper surfacing colours, linoleum, and oil and water paint colours
Acid dyestuffs .	(1) Quinoline yellow S .	*Shade* —Pure greenish-yellow. *Uses* — Paper surfacing and printing ink colours

Class	Name	Remarks
	(2) Lissamine fast-yellow 2G S	*Shade* —Greenish-yellow, possessing good light fastness. *Uses* — Paper surfacing and printing ink colours
	(3) Naphthol yellow F Y S	*Shade* —Greenish-yellow *Uses* — Paper surfacing and printing ink colours
	(4) Tartrazine N S	*Shade* —Reddish-yellow *Uses* — Transparent printing ink and varnish colours
	(5) Metanil yellow Y.S	*Shade* —Reddish-yellow *Uses* — Wallpaper and paper surfacing colours
	(6) Citronine Y S	*Shade* —Reddish-yellow *Uses* — Wallpaper colours
	(7) Citronine R S	*Shade* —Reddish-yellow *Uses* — Wallpaper colours
	(8) Acid orange G S	*Shade.*—Bright yellowish-orange *Uses* — Printing ink colours, paper surfacing and oil colours
	(9) Lake orange O S	*Shade* —Bright orange *Uses* — Printing ink and paper surfacing colours
	(10) Acid orange R S	*Shade* —Bright reddish-orange. *Uses* — Printing ink and paper surfacing colours
	(11) Acid scarlet 4R S	*Shade* —Bright yellow-scarlet. *Uses* — Printing ink and paper surfacing colours
	(12) Lake scarlet G S	*Shade* —Bright yellowish-scarlet, possessing good light fastness *Uses* — Printing ink and paper surfacing colours.

CLASS	NAME.	REMARKS
	(13) Acid scarlet R S . ..	*Shade* —Bright bluish-scarlet *Uses* — Printing ink and paper surfacing colours.
	(14) Acid scarlet 2R.	*Shade* —Bluish-scarlet *Uses* — Printing ink and paper surfacing colours
	(15) Acid scarlet 3R. . .	*Shade* —Bluish scarlet. *Uses.*— Printing ink and paper surfacing colours
	(16) Lake scarlet 3B S.	*Shade.*—Scarlet top tone Fine bluish undertone *Uses* — Printing ink and oil colours Fast to light.
	(17) Brilliant carmine L S. ..	*Shade* —Brilliant bluish-crimson *Uses* — Printing ink and paper surfacing colours
	(18) Brilliant acid maroon S	*Shade* —Reddish maroon shade *Uses* — Principally used in nitrocellulose colours
	(19) Fast acid violet 2R S	*Shade* —Bright reddish-violet *Uses* — Printing ink colours
	(20) Pure Bordeaux B S .	*Shade* —Bluish-Bordeaux shade *Uses* — Printing ink and paper surfacing colours.
	(21) Gallocyanine B.D S .	*Shade* —Bluish-violet *Uses* — Printing ink and paper surfacing colours Good light fastness
	(22) Coomassie acid blue R L S	*Shade* —Reddish-blue *Uses* — Printing ink and paper surfacing colours
	(23) Coomassie violet R S .	*Shade* —Bright bluish-violet *Uses* — Printing ink and paper surfacing colours
	(24) Durocyanine violet R S ..	*Shade* —Bluish-violet. *Uses.*— Printing ink and paper surfacing colours

CLASS	NAME	REMARKS.
	(25) Soluble blue R.S ..	*Shade* —Reddish-blue *Uses* — Printing ink and paper surfacing colours
	(26) Soluble blue 3M.S	*Shade* —Reddish-blue *Uses* — Printing ink and paper surfacing colours
	(27) Pure soluble blue S	*Shade* —Bright blue shade *Uses* — Printing ink and paper surfacing colours
	(28) Alkali blue 4B S ..	*Shade* —Bright greenish-blue. *Uses* — Printing ink and paper surfacing colours
	(29) Solway fast blue B L conc	*Shade* —Greenish shade of blue of excellent light fastness *Uses* — Printing ink and paper surfacing colours
	(30) Lake blue A.S ..	*Shade* —Bright greenish-blue. *Uses* — Paper surfacing and wallpaper colours
	(31) Disulphine blue A.S	*Shade* —Bright greenish-blue *Uses* — Printing ink and paper surfacing colours
	(32) Disulphine blue V S	*Shade* —Bright greenish-blue. *Uses* — Printing ink and paper surfacing colours
	(33) Lissamine green V S. .	*Shade* —Bright bluish-green. *Uses* — Printing ink and paper surfacing colours
	(34) Acid green G S. .	*Shade* —Bright bluish-green. *Uses* — Printing ink and paper surfacing colours
	(35) Lissamine green S F.	*Shade* —Bright green shade *Uses* — Printing ink and paper surfacing colours.
	(36) Solway green G	*Shade* —Bluish-green of very good light fastness *Uses* — Printing ink colours, wallpaper and paper surfacing colours

CLASS	NAME	REMARKS
	(37) Naphthol green B S	*Shade.*—Yellowish-green of very good light fastness. *Uses.*—Printing ink colour, wallpaper and paper surfacing colours
	(38) Nigrosine G S crystals	*Shade*—Rich black. *Uses*—Printing ink and paper surfacing colours
Dyestuffs of the Eosin class	(1) Eosin 3Y S	*Shade*—Bright fiery scarlet. *Uses.*—Printing ink and paper surfacing colours
	(2) Eosin Y S	*Shade*—Bright crimson. *Uses.*—Printing ink and paper surfacing colours
	(3) Eosin B S	*Shade.*—Bluer shade than Eosin Y S. *Uses*—Printing ink and paper surfacing colours
	(4) Eosin 2B S.	*Shade*—Bluer shade than Eosin B S *Uses*—Printing ink and paper surfacing colours
	(5) Phloxine B S	*Shade*—Bright bluish-crimson. *Uses*—Printing ink and paper surfacing colours
Basic dyestuffs	(1) Acronol yellow T S	*Shade*—Bright greenish-yellow *Uses*—Printing ink and paper surfacing colours, wallpaper and distemper colours
	(2) Auramine O S	*Shade*—Bright yellow. *Uses*—Printing ink and paper surfacing colours, wallpaper and distemper colours
	(3) Bismarck brown R S	*Shade.*—Redder than Bismarck brown G S. *Uses*—Printing ink and paper surfacing colours, wallpaper and distemper colours.
	(4) Bismarck brown G S	*Shade*—Yellowish-brown. *Uses.*—Printing ink and paper surfacing colours, wallpaper and distemper colours.

CLASS	NAME	REMARKS
	(5) Acridine orange L P new	*Shade* —Yellowish-orange *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(6) Chrysoidine Y R P S	*Shade* —Yellowish-brown *Uses* — Printing ink and paper surfacing colours
	(7) Safranine T S	*Shade* —Bluish-crimson *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(8) Rhodyle 4G S	*Shade* —Bright bluish-crimson *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(9) Tannin pink C S	*Shade* —Bluer shade than Rhodyle 4G S *Uses* —Printing ink and paper surfacing colours, wallpaper and distemper colours
	(10) Magenta P S	*Shade* —Bright bluish-magenta shade. *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(11) Methyl violet 2B S	*Shade* —Reddish-violet *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(12) Methyl violet 10B L S	*Shade* —Bluish-violet *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(13) Indine blue 2R D S	*Shade* —Reddish-blue. *Uses* — Printing ink and paper surfacing colours, wallpaper colours

Class	Name.	Remarks
	(14) Victoria blue R S	*Shade* —Brilliant blue shade *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(15) Victoria blue B S	*Shade* —Greener than Victoria blue R.S *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(16) Methylene blue 2B S	*Shade* —Greenish-blue Fast to light *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(17) Acronol brilliant blue S	*Shade* —Bright greenish-blue *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(18) Turquoise blue G S	*Shade* —Very greenish-blue. *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(19) Malachite green crystals A.S	*Shade* —Bluish-green. *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours
	(20) Brilliant green crystals Y S .	*Shade* —Bluish-green *Uses* — Printing ink and paper surfacing colours, wallpaper and distemper colours

THE CLAYTON ANILINE COMPANY, LTD.
DYESTUFFS FOR LAKE MANUFACTURE

Class	Name	Remarks.
Insoluble colours with no lake forming properties	Lake yellow 2G. paste and powder .	*Shade* —Full greenish-yellow *Uses* — Printing inks, paper and wallpaper coating, and in distempers.

CLASS	NAME	REMARKS
	Lake red 2G paste and powder	*Shade* —Bright orange-red *Uses* — Fast to light printing inks, paper and wallpaper coating, oil and water paints, and linoleum.
	Aniline black powder	*Shade* —Rich, deep black *Uses* — Fast to light printing inks, paper and wallpaper coating, and in colouring linoleum and vulcanite
Partly soluble azo dyestuffs with lake forming properties	Signal red paste—yellow shade and blue shade and powder	*Shade* —Bright bluish-red as barium lake. Bluer shade as calcium lake *Uses* — Printing ink colours, oil and water paint colours, distemper colours, and also in colouring rubber
	Permanent red 4B. paste and powder	*Shade* —Bright orange-red as barium lake Bluer shade as calcium lake *Uses* — Fast to light printing ink colours, oil and water paint colours, paper and wallpaper coating, distemper colours, and linoleum and rubber colours.
	Permanent red B powder	*Shade* —Bright orange-red as barium lake (yellower than "4B.") Bluer shade as calcium lake *Uses* — Fast to light printing ink colours, oil and water paint colours, paper and wallpaper coating colours, and linoleum and rubber colours.
Acid Dyestuffs	Quinoline yellow ..	*Shade* —Pure greenish-yellow, as barium lake *Uses* — Printing ink and paper coating colours

CLASS	NAME	REMARKS
	Naphthol yellow S	*Shade* —Full bright yellow, as barium lake *Uses* — Printing ink and paper coating colours
	Tartrazine	*Shade* —Full bright yellow, as barium lake. *Uses* — Printing ink and paper coating colours
	Azo yellow I	*Shade* —Full yellow *Uses* — Paper and wallpaper coating colours
	Citronine O O O	*Shade* —Full reddish-yellow *Uses* — Paper and wallpaper coating colours
	Orange M N.O	*Shade* —Full orange-green *Uses* — Paper and wallpaper coating colours
	Chrome fast yellow B R. conc (acid mordant colour)	*Shade* —Full orange-yellow *Uses* --Paper and wallpaper coating colours
	Ponceau 4G	*Shade* —Bright yellowish-orange *Uses* — Paper and wallpaper coating colours
	Orange I I L	*Shade* —Bright orange *Uses* — Paper and wallpaper coating colours
	Acid scarlet 2R	*Shade* —Full bluish-scarlet *Uses* — Paper and wallpaper coating colours
	Brilliant scarlet R	*Shade* —Full red *Uses* — Paper and wallpaper coating colours
	Ponceau 2G	*Shade* —Bright yellowish-red *Uses* — Paper and wallpaper coating colours

Class	Name	Remarks
	Lake carmine L	*Shade* —Bright carmine shade *Uses* — Paper and wallpaper coating colours
	Fast acid violet A 2R	*Shade* —Full reddish-violet *Uses* — Paper and wallpaper coating colours
	Benzyl violet 5B N	*Shade* —Full bright violet *Uses* — Paper and wallpaper coating colours
	Acid violet 4B N S	*Shade* —Full bright violet, bluer than " 5B N " *Uses* — Printing ink colours, paper and wallpaper coating colours
	Kiton blue A	*Shade* —Bright greenish-blue *Uses* — Printing ink colours, paper and wallpaper coating colours
	Benzyl green B	*Shade* —Bright bluish-green *Uses* — Printing ink colours, paper and wallpaper coating colours
	Acid black H A	*Shade* —Full blue-black *Uses* — Printing ink colours, paper and wallpaper coating colours
	Nigrosine K	*Shade* —Full black *Uses* — Printing ink colours, paper and wallpaper coating colours
	Nigrosine B	*Shade* —Slightly redder than " K " brand *Uses* — Printing ink colours paper and wallpaper coating colours
s	Nigrosine R	*Shade* —Slightly redder than " B " brand *Uses* — Printing ink colours, paper and wallpaper coating colours

Class	Name.	Remarks
Eosine class	Eosine Y S	*Shade* —Full brilliant fiery red *Uses* — Printing ink colours, paper and wallpaper coating colours
	Eosine 2Y S	*Shade* —Full brilliant fiery red *Uses* — Printing ink colours, paper and wallpaper coating colours
Basic dyestuffs	Auramine O	*Shade* —Full bright yellow *Uses* — Paper and wallpaper coating colours, and distemper colours
	Chrysoidine G crystals	*Shade* —Yellowish-orange *Uses* — Paper and wallpaper coating colours, and distemper colours
	Chrysoidine R crystals	*Shade* —Slightly redder than " G " brand *Uses* — Paper and wallpaper coating colours, and distemper colours
	Rhodamine 6G extra	*Shade* —Brilliant pink *Uses* — Printing ink colours, paper and wallpaper coating colours, and distemper colours
	Rhodamine B extra	*Shade* —Brilliant bluish-pink *Uses* — Printing ink colours, paper and wallpaper coating colours, and distemper colours
	Magenta powder and crystals	*Shade* —Full Bordeaux shade *Uses* — Printing ink colours, paper and wallpaper coating colours, and distemper colours
	Methyl violet 2B conc	*Shade* —Full bright violet *Uses* — Printing ink colours, paper and wallpaper coating colours, and distemper colours

Class	Name	Remarks
	Violet 5B O	*Shade* —Rather bluer than methyl violet 2B *Uses* — Printing ink colours, paper and wallpaper coating colours, and distemper colours
	Victoria blue 4R	*Shade* —Bright reddish-blue *Uses* — Printing ink colours, paper and wallpaper coating colours, and distemper colours
	Victoria blue R	*Shade* —Bright pure blue *Uses* — Printing ink colours, paper and wallpaper coating colours, and distemper colours
	Victoria blue B	*Shade* —Slightly greener than " R " brand *Uses* — Printing ink colours, paper and wallpaper coating colours, and distemper colours
	Methylene blue G	*Shade* —Bright greenish-blue. *Uses* — Printing ink colours, paper and wallpaper coating colours, and distemper colours
	Malachite green crystals	*Shade* —Bright bluish-green *Uses* — Printing ink colours, paper and wallpaper coating colours, and distemper colours
	Brilliant green crystals	*Shade* —Rather yellower than malachite green. *Uses* — Printing ink colours, paper and wallpaper coating colours, and distemper colours.
Chlorantine fast colours—non-bleeding colours for cellulose dopes	Chlorantine fast yellow	
	5G L	*Shade* —Full greenish-yellow
	4G L	,, Full greenish-yellow
	R L	,, Bright yellow
	Chlorantine fast orange	
	G	,, Full orange-yellow
	T R L	,, Full yellowish-orange
	2R L	,, Full orange

Class	Name	Remarks
	Chlorantine fast brown	
	R.L	*Shade* —Bright orange brown
	B R L	,, Rich umber shade
	Chlorantine fast red	
	5G L	,, Bright rich red
	K	,, Deep bluish-red
	6B L	,, Deep bluish-red
	Chlorantine fast Bordeaux	
	B L	, Full Bordeaux shade
	Chlorantine fast violet	
	R L	,, Full maroon shade
	B L N	,, Full reddish-violet
	4B L N	,, Little greener than " B L N " brand
	5B L	,, Full bluish-violet.
	Chlorantine fast blue	
	R L	,, Deep reddish-blue
	2G L	, Greener than " R L " brand
	4G L	,, A little greener than the " 2G L " brand
Direct dyestuffs	Stilbene yellow 8G	*Shade* —Full yellow *Uses* — Paper and wallpaper coating colour
	Stilbene yellow 2G	*Shade* —Full reddish-yellow *Uses* — Paper and wallpaper coating colours
	Direct yellow R	*Shade* —Full reddish-yellow. *Uses* — Paper and wallpaper coating colours, oil paint colours and cellulose dope colours
	Direct fast scarlet S E	*Shade* —Full red *Uses* —- Paper and wallpaper coating

AUTHOR'S NOTE —The above comprehensive list includes, of course, those dyes which yield lakes of only moderate fastness to light, but which are used on account of their brightness of shade, their comparative cheapness, or for other economic considerations

EMCO DYESTUFFS LTD

DYESTUFFS FOR LAKE MANUFACTURE

CLASS	NAME	REMARKS
Insoluble azo dyestuffs with no lake-forming properties	(1) Helio fast red R B L paste and powder	*Shade* —Brilliant scarlet. *Uses* — Fast to light printing ink colours, wallpaper and paper surfacing colours, oil, distemper and water paints
	(2) Permanent red R paste and powder	*Shade* —Brilliant yellowish shade of red *Uses* — Fast to light wallpapers and surfacing colours, oil and water paint colours, printing ink and linoleum colours
	(3) Permanent red 2G paste and powder	*Shade* —Orange-red *Uses* — Fast to light printing ink colours, wallpaper and paper surfacing colours, oil and water paint colours and linoleum colours
	(4) Lithol fast scarlet G paste and powder	*Shade* —Brilliant yellowish shade of red *Uses* — Fast to light wallpaper and surfacing colours, oil and water paint colours, printing ink and linoleum colours
	(5) Permanent red 4R paste and powder	*Shade* —Brilliant scarlet *Uses* — Fast to light printing ink and linoleum colours, wallpaper and paper surfacing colours, oil and water paint colours
	(6) Permanent yellow 5G. paste and powder	*Shade* —Extra greenish-yellow. *Uses* — Fast and light printing ink colours, wallpaper and paper surfacing colours, oil and water paint colours and distemper colours

CLASS	NAME	REMARKS
	(7) Permanent yellow G paste and powder	*Shade* —Greenish-yellow *Uses* — Fast to light printing ink colours, wallpaper and paper surfacing colours, oil and water paint colours and distemper colours
	(8) Permanent yellow G R paste and powder	*Shade* —Golden-yellow *Uses* — Fast to light printing ink and distemper colours, oil and water paint colours, wallpaper and paper surfacing colours
	(9) Pigment green B paste and powder	*Shade* —Yellowish-green *Uses* — Fast to light wallpaper and paper surfacing colours, distemper and cement colours
Insoluble or partially soluble azo dyestuffs which possess lake forming properties	(1) Permanent red B. paste or powder	*Shade* —Brilliant scarlet as barium salt, bluish-red as calcium salt *Uses* — Printing ink colours, oil and water paints, wallpaper and paper surfacing colours and linoleum colours
	(2) Permanent red 2B paste and powder	*Shade* —Brilliant Scarlet as barium salt, pure bluish-crimson as calcium salt *Uses* — Printing ink colours, oil and water paints, wallpaper, paper surfacing and linoleum colours
	(3) Permanent red 4B paste and powder	*Shade* —Fiery red as barium salt, pure bluish-carmine as calcium lake *Uses* — Printing ink colours, wallpaper and paper surfacing colours, linoleum, oil and water paint colours

Class	Name	Remarks
	(4) Lake red C paste	*Shade* —Bright yellowish-red possessing fine bluish undertone, barium salt, a rich bronze scarlet *Uses* — Printing ink, linoleum and rubber colours
	(5) Lake red D paste	*Shade* —Bright yellowish-red *Uses* — Printing ink colours
	(6) Lithol red R paste and powder	*Shade* —Bright bluish-red as barium salt, bluer shade as calcium salt *Uses* — Printing ink colours, oil and water paint colours, and distemper colours
	(7) Lithol rubine G paste or powder	*Shade* —Brilliant scarlet as barium salt Bluish-red as calcium salt *Uses* — Printing ink colours, oil and water paints, wallpaper and paper surfacing colours and linoleum colours
Acid dyestuffs	(1) Orange II	*Shade* —Bright orange *Uses* — Paper surfacing colours and transparent printing ink colours
	(2) Orange R	*Shade* —Redder than orange II *Uses* — Paper surfacing colours and printing ink colours
	(3) Ponceau R	*Shade* —Bright bluish-scarlet *Uses* — Printing ink and paper surfacing colours
	(4) Ponceau 2R	*Shade* —Bright bluish-scarlet *Uses* — Printing and paper surfacing colours

CLASS	NAME	REMARKS.
	(5) Ponceau 3R	*Shade* —Bright bluish-scarlet. *Uses* — Printing ink and paper surfacing colours
	(6) Ponceau R X.	*Shade* —Bright bluish-scarlet. *Uses* — Printing ink and paper surfacing colours
	(7) Pigment scarlet G	*Shade* —Bright yellowish-scarlet Good fastness to light *Uses* — Printing ink and paper surfacing colours
	(8) Pigment scarlet 3B	*Shade* —Scarlet top tone, fine bluish undertone. *Uses* — Fast to light printing ink and oil colours
	(9) Nigrosine W S.	*Shade* —Rich black *Uses* — Printing ink and paper surfacing colours
Basic dyestuffs	(1) Methyl Violet 2B E	*Shade* —Reddish-violet *Uses* — Printing ink and wallpaper colours, paper surfacing and distemper colours
	(2) Victoria blue R E	*Shade* —Brilliant blue *Uses* — Printing ink and wallpaper colours, paper surfacing and distemper colours
	(3) Turquoise blue G E	*Shade* —Very greenish-blue *Uses* — Printing ink and wallpaper colours, paper surfacing and distemper colours
	(4) Brilliant green crystals	*Shade* —Bluish-green *Uses* — Printing ink and wallpaper colours, paper surfacing and distemper colours

L B HOLLIDAY & CO LTD
DYESTUFFS FOR LAKE MANUFACTURE

Class	Name of Dyestuff	Usual Precipitant	Shade of Lake	General Uses and Properties
Basic dyestuffs	Auramine O conc	On china clay or barytes, or both, with tannic acid and tartar emetic, or on green earth without further assistance	Greenish-yellow	Wallpapers, covered papers, and distempers The fastness to light generally is only moderate but much better fastness is obtained on a substratum of green earth Malachite and Brilliant greens are very important colours on green earth as lime greens
	Chrysoidine Y Powder		Orange	
	Chrysoidine R Powder		Orange	
	Bismarck brown R conc		Brown	
	Brilliant safranine G R conc		Pink	
	Brilliant safranine B R conc		Pink	
	Magenta superfine		Magenta	
	Brilliant heliotrope 2R		Heliotrope	
	Methyl violet 2B conc		Violet	
	Methyl violet 4B conc.		Violet	
	Victoria blue B		Bright blue	
	Victoria blue R.		Bright blue	
	Methylene blue, 1814		Greenish-blue	
	Methylene blue 2B conc		Greenish-blue	
	New Blue R ex. conc		Dark blue	
	Malachite green crystals		Bluish green	
	Brilliant green crystals		Green	
Soluble acid, azo dyestuffs, alizarines and pryazolones, etc	Fast light yellow 3G	With barium chloride or (more rarely) calcium chloride	Greenish-yellow	For wallpapers, covered papers, and lithographic inks
	Metanil yellow		Reddish-yellow	
	Indian yellow		Reddish-yellow	
	Tartar yellow F S		Greenish-yellow	
	Naphthol yellow		Greenish yellow	Excellent fastness to light
	Orange II		Orange .	Light
	Orange R O		Redder orange	
	New Ponceau 4R conc		Scarlet	Good fastness to light
	Brilliant crocein L B H New		Scarlet	

CLASS	NAME OF DYESTUFF	USUAL PRECIPITANT	SHADE OF LAKE	GENERAL USES AND PROPERTIES
	Brilliant azo fuchsine 2G F ex	With barium chloride or (more rarely) calcium chloride	Scarlet and crimson	Moderately good fastness to light
	Brilliant azo fuchsine 10 B.		Scarlet and crimson	Moderately good fastness to light
	Alizarine brilliant violet R		Reddish-violet	Very good fastness to light
	Acid milling violet 6B		Bluish-violet	Moderate fastness to light
	Brilliant milling violet S4B		Reddish-violet	Moderate fastness to light
	Alizarine brilliant Blue B		Blue	Excellent fastness to light
	Alizarine brilliant greens		Green	Excellent fastness to light
	Soluble blues		Blues	Good fastness to light
	Patent blues		Greenish-blues	Moderate fastness to light
	Monochrome yellow 2R		Golden yellow	Precipitates without other mordant, quarter as much concentrated basic blue or green for deep olive-greens
	Nigrosines		Greys	Very good fastness to light
	Indulines		Blue greys	Very good fastness to light
Soluble substantive azo and other colours	Diazamine fast yellow H	With barium chloride or (more rarely) calcium chloride	Greenish-yellow	Excellent to light
	Paramine fast yellow 3G		Greenish-yellow	,, ,, ,,
	Paramine yellow R		Medium yellow	,, ,, ,,
	Chrysophenine G		Bright medium yellow	,, ,, ,,
	Paramine brown G		Yellowish-brown	Moderate to light
	Paramine blue 2B new		Blue	,, ,, ,,
	Paramine sky blue F F		Sky blue	,, ,, ,,
	Paramine fast violet N		Violet	Good to light
	Paramine green G		Green	,, ,, ,,
	Paramine blacks		Black	,, ,, ,,

Class	Name of Dyestuff	Usual Precipitant	Shade of Lake	General Uses and Properties
Eosine colours	Eosin A.	Lead acetate or (more rarely) barium chloride	Bright pink	For wallpapers, covered papers, and lithographic inks Moderate fastness to light
	Eosin 3G		Bright pink	
	Erythrosin		Bluer shade	
	Phloxine P		Bluer still	
	Rose Bengal		Bluish shade	
	Bromofluorescein		Red with bluish undertone	
Pigment colours	Lithol red R	Calcium chloride or barium chloride	Red	For lithographic inks and paints Excellent to light Excellent fastness to oil

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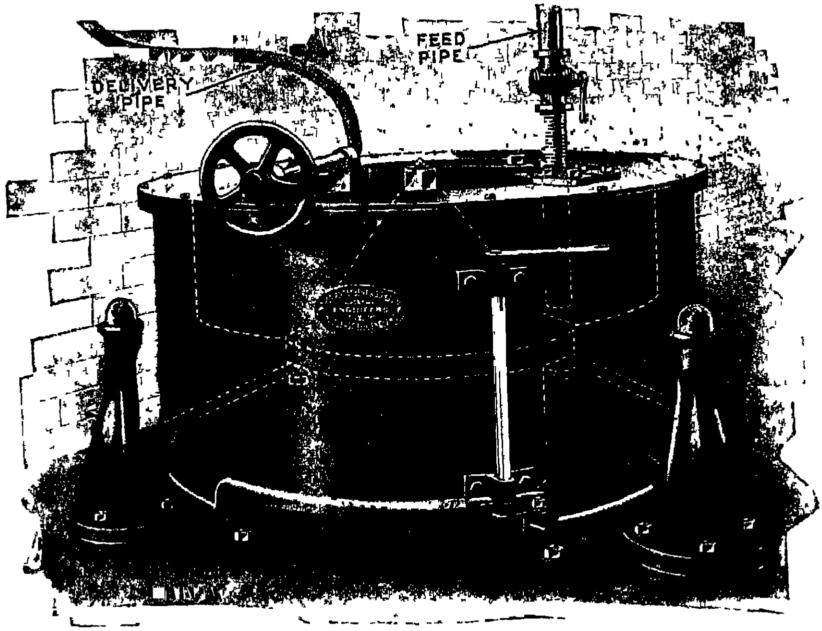

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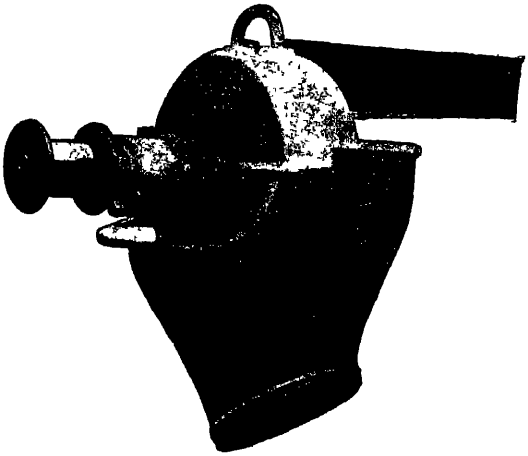

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